I found 37·5 per cent. of phosphorus, while the formula $H_4Am_2PO_2$ requires—

$$
\begin{array}{lcrcr}
2H & = & 2 & = & 2·41 \\
Am & = & 18 & = & 21·69 \\
P & = & 31 & = & 37·35 \\
2O & = & 32 & = & 38·55 \\
 & & \overline{83} & & \overline{100·}
\end{array}
$$

Under the influence of heat decomposition takes place, ammonia and phosphoretted hydrogen being evolved (the latter is for the most part not spontaneously inflammable), and a glassy mass of phosphoric acid remaining.

As I found that 100 parts of the salt give 55·2 of residue containing 20·16 phosphorus, it seems that the residue is formed by—

$$\left\{\begin{array}{l} H_4P_2O_7 \\ 2HPO_3 \end{array}\right\}$$

because that supposition would require 57·67 per cent of residue = 21·34 P.

$$7H_4AmPO_2 = H_6P_4O_{13} + H_2O + 7NH_3 + 3PH_3 + 2H_2.$$

Hypophosphite of Barium.

The methods of preparing this salt are well known, but the crystals are very rarely well formed. They belong to the monoclinic system, and show combinations of the faces—

$$\frac{o}{2} = a : b : \tfrac{1}{2}c \qquad p = a : b$$

$$\frac{o'}{2} = a' : b : \tfrac{1}{2}c \qquad q = b : c$$

$$s = \tfrac{1}{2}a : b : c \qquad r = a : c :$$

$$r' = a' : c :$$

$$\frac{r'}{2} = 2a' : c : \infty b$$

$$a : b : c = 1·575 : 1 : 2·00$$

$$o = 79° \; 40'$$

	Calculated.	Observed.
$p : p =$	65 40′	—
$c =$	95′ 35′	—
$q : q =$	—	× 53° 40′
$a =$	94° 30′	94° 30′
$a : c =$	—	× 100° 20′
$r =$	—	× 145° 50′
$r' =$	137° 57′	137° 30′

	Calculated.	Observed.
$c : r =$	$134° 30'$	$134° 15'$
$r' =$	$121° 43'$	$122° 30'$
$\frac{r'}{2} =$	$144° 49'$	$145° 8'$
$p : r =$	$116° 39'$	$116° 30'$
$r' =$	$113° 44'$	—
$q : r =$	$108° 27'$	$109° 15'$ appr.
$r' =$	$103° 44'$	$104° 20'$
$s : s =$	$111° 32'$	$112° 0'$
$a =$	$141° 2'$	$140° 55'$
$c =$	$114° 35'$	$114° 42'$
$q =$	$133° 37'$	$133° 10'$

The crystals are prisms a, c, r, r', terminated by q and s, the faces p, $o\frac{1}{4}$, $o'\frac{1}{2}$ being extremely small. They are colourless and transparent, unalterable in air and at temperatures under 100°.

My own experiments agree with those of Wurtz with regard to the composition of the salt, which contains 1 molecule of water.

$$H_4BaP_2O_4 + aq.$$

			Found.
4H =	4 =	1·40	—
Ba =	137 =	48·07	48·01
2P =	62 =	21·75	22·56
4O =	64 =	22·47	—
aq. =	18 =	6·31	6·28
	285	100·	

100 parts treated with nitric acid yielded 103·5 metaphosphate of barium, BaP_2O_6.

When the anhydrous salt is heated in closed vessels, it becomes reddish, gives off inflammable phosphoretted hydrogen, yields a small quantity of yellow phosphorus, and leaves a residue weighing 87·0—87·4 per cent. Hydrochloric acid dissolves it, leaving only a certain quantity of red phosphorus. The composition of the whole was indicated by several analyses, one of which gave—

Phosphorus, free	1·50 =	—
"	12·41 =	14·45
Barium	50·97 =	59·34
Oxygen	22·52 =	26·21
	87·40	100·

Such is the composition of a substance hitherto considered as a

pyrophosphate. But the difference, though not great, is evident. In pyrophosphate Ba : P = 1 : 1 atom; 59·34 Ba would then require 13·43 P, while the proportion of the two elements actually found is 13 : 14.

Another test for the assumption that the phosphate cannot be pure pyrophosphate is to be found in its quantity.

$H_4BaP_2O_4$ would give 83 per cent. $Ba'_2P_2O_7$, whereas the experiments have given 85 per cent., or a little more (without the unmixed free phosphorus).

It may therefore be stated that the substance, generated by ignition of hypophosphite of barium is—

$$Ba_{13}P_{14}O_{48} = \left\{ \begin{matrix} 6Ba_2P_2O_7 \\ BaP_2O_6 \end{matrix} \right\}$$

or 6 mol. of pyrophosphate and 1 mol. of metaphosphate. 100 parts of the anhydrous salt should then give 85·9 of these phosphates, and 100 parts of them should contain—

P	14·55
Ba	59·73
O	25·72
	100·

agreeing well with the results of analysis.

Hypophosphite of barium then gives by the action of heat—

$$13H_4BaP_2O_4 = Ba_{13}P_{14}O_{48} + 12H_3P + 4H_2 + 4H_2O.$$

As a part of phosphorus appears in the free state, it is evident that the proportion of free hydrogen will be greater. The water produced being equal to 2 per cent. of the salt, it would be nearly impossible to determine it in a satisfactory manner.

We shall see in the course of these researches, that pure pyrophosphate is not produced by any hypophosphite, but the barium salt yields when heated a residue which approximates closely thereto. It will therefore easily be understood that H. Rose 45 years ago was led to erroneous conclusions on this point, by not extending his quantitative experiments on the nature of the phosphates formed by ignition of hypophosphites to a greater number of salts.

Hypophosphite of Strontium.

By evaporating a solution of carbonate in free hypophosphorous acid, white crystalline crusts are obtained, much less soluble than the barium salt. They contain $H_4SrP_2O_4$ + aq., and give off 7·64 per cent. of water at 200°.

100 parts of the anhydrous salt, decomposed by heat, gave 88·9 of a residue containing 39·32 strontium, 16·4 phosphorus in combination and 3·06 in the free state. Supposing the atomic ratio of Sr : P to be 7 : 8, the substance would be—

$$Sr_7P_8O_{27} = \left\{ \begin{matrix} 3Sr_2P_2O_7 \\ SrP_2O_6 \end{matrix} \right\}$$

and the process of decomposition—

$$7H_4SrP_2O_4 = Sr_7P_8O_{27} + 6H_3P + 4H_2 + H_2O.$$

Hypophosphite of Calcium.

According to Wurtz, the crystals of this salt are anhydrous, and I myself have obtained the same result. No loss at 200°; Ca = 23·75, P = 36 55 per cent., corresponding with the formula $H_4CaP_2O_4$

The system of crystallisation is monoclinic; observed faces—

$$\begin{array}{llll} o' = a' : b : c & & a = a : \infty b : \infty c \\ s' = 3a' : b : c & & b = b : \infty a : \infty c \\ 3p = 3a : b : \infty c & & c = c : \infty a : \infty b \\ r' = a' : c : \infty b & & \end{array}$$

$$a : b : c = 0{\cdot}8693 : 1 : 1{\cdot}200$$
$$o = 75° \; 12'$$

	Calculated	Observed. Rammelsberg	Observed. Schabus
$o' : o' =$		× 103° 40′	103° 56′
$s' : s' =$	80° 52′	—	—
$3p : 3p =$	43° 16′	—	—
$a : c =$	—	× 103° 40′	—
$r' =$	139° 20′	—	—
$o' : a =$	—	× 126° 25′	126° 35′
$c =$	110° 1′	—	—
$s' : a =$	97° 44′	99° 30′	99° 37′
$c =$	125° 24′	125° 50′	—
$o' =$	151° 3′	152° 30′	—

The crystals become tabular by the extension of face a; they are transparent and flexible, and undergo no change on exposure to the air.

Their behaviour when heated is like that of the strontium salt; they gave 79·35—79·8 per cent. phosphates, and 4·4 of free phosphorus. The phosphates contained Ca 29 22—29·43, and P 25·79—26·04; they are consequently—

$$Ca_7P_8O_{27} = \left\{ \begin{matrix} 3Ca_2P_2O_7 \\ CaP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Magnesium.

Very fine regular octahedrons, with the faces of the cube, containing 6 mol. of water, $H_4MgP_2O_4 + 6aq.$, according to the experiments of H. Rose, Wurtz, and my own.

After drying at 200°, the salt yields, when heated, a gas which is for the most part not spontaneously inflammable. The white residue becomes reddish on cooling, and dissolves easily in acids, while a small portion of phosphorus is separated. Experiment gave 4·2 P and 80·7 phosphates = Mg 16·15, P 22·63. Hence we may calculate for the phosphates—

$$Mg_5P_6O_{20} = \left\{ \begin{matrix} 2Mg_2P_2O_7 \\ MgP_2O_6 \end{matrix} \right\}$$

and the process will be—

$$5H_4MgP_2O_4 = Mg_5P_6O_{20} + 4H_3P + 4H_2.$$

Hypophosphite of Zinc.

Isomorphous with the former, it has the composition $H_4ZnP_2O_4 + 6aq.$, as Wurtz has determined by analysis.

Decomposed by heat, the anhydrous salt leaves 85·38 per cent. = Zn 33·86, P 18·94, O 32·58, besides 0·88 free phosphorus, or the same phosphates as the magnesium salt—

$$Zn_5P_6O_{20} = \left\{ \begin{matrix} 2Zn_2P_2O_7 \\ ZnP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Manganese.

Very small reddish crystals, the form of which I could not determine, easily soluble; containing, according to Wurtz, 8·86 per cent. of water (9·85 in my own experiment), and therefore $H_4MnP_2O_4 + aq.$

On heating the anhydrous salt a gas evolved, which for the most does not take fire on coming in contact with the air. The white residue becomes reddish on cooling, contains 2·82 of free phosphorus and 81·07 of phosphates = Mn 29·73, P 20·14, O 31·20; it is therefore like the former—

$$Mn_5P_6O_{20} = \left\{ \begin{matrix} 2Mn_2P_2O_7 \\ MnP_2O_6 \end{matrix} \right\}$$

Hypophosphite of Cerium.

By decomposing the barium salt with sulphate of cerium, white crystalline crusts are obtained, difficultly soluble in water. Analysis gave Ce 39·22, P 26·43, aq. 4·81, corresponding to the formula, $3H_4CeP_2O_4 + 2aq.$

The products of decomposition by heat were 2·87 free phosphorus and 84·95 phosphates = Ce 41·44, P 16·07, which agrees with—

$$Ce_7P_8O_{27} = \left\{ \begin{matrix} 3Ce_2P_4O_7 \\ CeP_2O_6 \end{matrix} \right\}$$

like the strontium and calcium salts.

Hypophosphite of Cadmium.

This salt is very much like the cerium or strontium salt, but contains no water of crystallisation. It gives a greyish or reddish residue = 0·34 phosphorus, and 86·5 phosphates = Cd 46·28 and P 14·30, or like the former, 3 mol. of pyrophosphate and 1 mol. of metaphosphate of cadmium.

Hypophosphite of Lead.

The lead salt forms thin splendent scales, dissolves with difficulty in water, is anhydrous, and, according to H. Rose, contains $H_4PbP_2O_4$.

The product of decomposition appears white, and contains no free phosphorus. I obtained 89·48 per cent. = Pb 60·56 and P 10·18, or

$$Pb_9P_{10}O_{34} = \left\{ \begin{matrix} 4Pb_2P_2O_7 \\ PbP_2O_6 \end{matrix} \right\}$$

Hence the process must be

$$9H_4PbP_2O_4 = Pb_9P_{10}O_{34} + 8H_3P + 4H_2 + 2H_2O.$$

Wurtz has stated that the salt is changed by an excess of oxide of lead into phosphite, believed by H. Rose to be a basic salt.

Hypophosphite of Cobalt.

Very fine crystals, brownish, regular octahedrons, isomorphous with the magnesium and zinc salt, containing 6 mol. of water. Now Wurtz has determined by analysis, and I have also found, that 36·2 per cent. of water goes off at 120°—130°. If the temperature rises to 150°, decomposition begins, the salt becomes black, and the evolved gas does not for the most take fire spontaneously in the air. From the anhydrous salt 91·7 per cent. of residue were obtained.

This substance treated with strong nitric acid, is oxidized, and after evaporation its weight is augmented by 12·9 per cent. Hence it is evident that the whole is a mixture of phosphate and *phosphide* of cobalt, containing Co 34·04 P 29·95, and O 36·01. The atomic ratio of Co : P is therefore 3 : 5 and Co : O = 1 : 4, as in hypophosphite, and I suppose the substance to be

$$Co_3P_5O_{12}, \text{ or } \left\{ \begin{matrix} 2CoP_2O_6 \\ CoP \end{matrix} \right\}$$

and the process

$$3H_4CoP_2O_4 = Co_3P_5O_{12} + H_3P + H_8.$$

H. Rose, in determining only the amount of cobalt in the residue, supposed it to be a mixture of pyro- and metaphosphate, coloured by black phosphorus; but from my own experiments I am convinced that such an admission does not agree with the behaviour of the substance and its composition.

Hypophosphite of Nickel.

Green crystals of the same form, combined with the faces of the cube; their isomorphism, and the analyses made by Wurtz and by myself, establish the formula, $H_4NiP_2O_4 + 6$ aq. At 100° the water is driven off; at 140° decomposition takes place; no inflammable gas is evolved and a black residue = 92·3 per cent. remains. As I found that this salt is exactly like the cobalt salt, and contains Ni 33·49, P 30·88, and O 35 63, it is evidently of the same nature, *i e.*, $\left\{ \begin{matrix} 2NiP_2O_6 \\ NiP \end{matrix} \right.$.

Hypophosphite of Uranium.

When the yellow precipitate of uranium-nitrate by ammonia is digested with free hypophosphorous acid, it is changed into a yellow crystalline salt, very difficultly soluble in water.

100 parts gave 39 parts of water, at temperatures of 100°—200°. By treatment with nitric acid, 102 4 of metaphosphate were obtained, proved by analysis to be UPO_4; therefore the hypophosphite is $H_4(U_2O_2)P_2O_4$ + aq., containing like the other salts, the radical uranyl, U_2O_2, and U : O = 1 : 3, while in the foregoing salts the atomic ratio P : O is always 1 : 4.

For this reason the uranyl hyposulphite differs essentially from the other hypophosphites in its decomposition by heat. No phosphorus is evolved, only hydrogen being set free; the uranyl salt is changed into a uranous salt, and the remaining product contains U : P : O = 1 : 1 : 3, like the hypophosphite itself. The process of decomposition, or the disengagement of hydrogen, is accompanied by a detonation, and the residue is a very porous mass of greenish colour. It dissolves in nitric acid, by which it is oxidized. I found U 61·37 and P 13·74 per cent., or UPO_3, and hence suppose the whole to be $\left\{ \begin{matrix} 3U_2P_2O_7 \\ UP_2O_6 \\ U_2P \end{matrix} \right\}$, or a mixture of pyro-phosphate, metaphosphate, and phosphide of uranium.

$$H_4(U_2O_2)P_2O_4 = 2UPO_3 + 2H_2.$$

The product of oxidation of UPO_3 by nitric acid is uranyl metaphosphate, $UPO_4 = (U_2O_2)P_2O_6$.

The results of my experiments on hypophosphites are in general the following:—These salts crystallise anhydrous (Tl, Ca, Cd, Pb), or, combined with water, the amount of which is 1 mol. (Na, Li, Ba, Sr, Mn, U), or 6 mol. (Mg, Zn, Ni, Co).

All are decomposed by heat.

1. The ordinary manner is that *pyrophosphate and metaphosphate* are formed, but the relative quantities of the two vary from 1 : 1 mol. (Na, Tl) to 2 : 1 mol. (Mg, Zn, Mn), 3·1 mol (Sr, Ca, Ce, Cd), 4 : 1 mol. (Pb), and 6 : 1 mol. (Ba).

2. *Metaphosphate and phosphide* are formed. (The nickel and cobalt salts.)

3. *Pyrophosphate, metaphosphate, and phosphide* remain. (The uranyl salt)

It is now easy to understand the difference between my results and those of H. Rose. This celebrated chemist had directed his attention principally to the nature of the phosphoretted hydrogen produced by these salts; his analytical researches on the remaining products were incomplete, and he had not studied those of the alkali-salts, which would have shown him that they are not at all pure pyrophosphates.

The gaseous products of the decomposition of hypophosphites being always a mixture of hydrogen and phosphoretted hydrogen, the inflammability of the gas is of no importance, and seems to vary according to circumstances. I also believe that the separation of phosphorus is due to the process itself, and does not depend on the decomposition of phosphoretted hydrogen, for I observed very often that phosphorus appears at the beginning of the process, while the temperature is not sufficient for the decomposition of phosphoretted hydrogen.

Phosphorous and hypophosphorous acid, phosphites and hypophosphites, are very much alike, notwithstanding that an essential difference exists in the products of their decomposition by heat. Phosphites give pure pyrophosphates, or a mixture of those salts with phosphides (Co, Pb, Mn, Zn), in consequence of the ratio of $R'' : H = 1 : 2$ or $1 : 1$. Phosphites leave no phosphorus: therefore in the products, $R'' : P = 1 : 1$, as in the original salts. They also give only hydrogen, while hypophosphites give hydrogen and phosphoretted hydrogen, the uranyl salt being the only one which resembles the phosphites in this respect.

The whole of the oxygen of phosphites is contained in the newly formed pyrophosphate, consequently water is never set free. The same takes place only in those hypophosphites which give

$$\left\{ \begin{matrix} R'_4P_2O_7 \\ R'PO_3 \end{matrix} \right\} \text{ or } \left\{ \begin{matrix} 2R''_2P_2O_7 \\ R''P_2O_6 \end{matrix} \right\}$$

or in the salts of Co, Ni, U, which yield phosphates and phosphides. In the other cases a certain portion of the oxygen is required to form a relatively small quantity of water.

II.—*On the Reducing Power of Phosphorous and Hypophosphorous Acid and their Salts.*

By C. Rammelsberg.

Phosphorous Acid and Silver-Salts.—By employing an excess of nitrate of silver, I found that 1 mol. of H_3PO_3 reduces 1 at. of Ag, while H becomes free.

$$\begin{aligned} H_3 + PO_3AgNO_3 : H_2O = {} & H_2PO_4 \\ & + HNO_3 \\ & + Ag + H. \end{aligned}$$

Hypophosphite of Barium and Silver-Salts.—1 mol. $H_4BaP_2O_4$, with an excess of nitrate, gave 5 Ag, and with sulphate of silver, 5·5 Ag. Admitting 6 Ag we should have

$$\begin{aligned} H_4BaP_2O_4 + 6AgNO_3 + 4H_2O = {} & 2H_3PO_4 \\ & + 4HNO_3 \\ & + BaN_2O_6 \\ & + 6Ag + 2H \end{aligned}$$

The reducing power of the molecules H_3PO_3 and H_3PO_2 seems to be $= 1 : 3$.

Phosphorous Acid and Copper Salts.—An excess of H_3PO_3 decolorises the solution, protoxide of copper being formed. When the sulphate of copper is prevalent, metallic copper is separated, after boiling for some time, and I found that for 3 at. of P 1 at. of Cu is reduced

$$\begin{aligned} 3H_3PO_3 + CuSO_4 + 3H_2O = {} & 3H_3PO_4 \\ & + H_2SO_4 \\ & + Cu + 4H \end{aligned}$$

Phosphite of barium is not changed by boiling with a solution of copper; when free sulphuric acid is added, a very small quantity of the metal is precipitated.

Hypophosphorous Acid and Copper Salts.—Wurtz has published his experiments on this subject, and the very interesting formation of HCu. H. Rose asserted (*Pogg. Ann*, 58, 212), that the reduction of copper was not accompanied by evolution of free hydrogen.

Hypophosphite of barium and an excess of sulphate of copper yield the reduction only at the boiling point of the liquid. I found Ba : Cu $= 1 : 2$ atoms. Hence it is evident that hydrogen is evolved.

But if free sulphuric acid is added, the reduction begins below 100°, and the quantity of the metal is only *half* what it was in the preceding case.

The two processes must be:

$$H_4BaP_2O_4 \text{ with } 2CuSO_4 \text{ and } 4H_2O \text{ gives } 2Cu + 4H$$

and

$$H_4BaP_2O_4 \text{ with } CuSO_4 \text{ and } 7H_2O \text{ gives } Cu + 6H.$$

The hydrogen is evolved with great rapidity.

Hypophosphite of sodium with an excess of copper-salt gives Na : Cu = 1 : 1 at., but the reaction requires continued boiling.

III.—*On the Action of Charcoal on Organic Nitrogen.*

By Edw. C. C. Stanford, F.C.S.

At the Exeter meeting of the British Association in 1869, I read a paper in the Chemical Section proposing a new method of dealing with excretal matters, fish offal, and other offensive nitrogenous substances, so as to secure the whole of their manurial value in an inoffensive form. The process is simply mixing the material with charcoal, which at once removes all odour. The mixture may be stored, and gradually becomes quite dry. It is then passed through re-burning retorts, when the whole of the nitrogen comes off as ammonia; this is neutralised with an acid, and can then be evaporated with the residual charcoal from the retorts, thus forming a general process void of all offence. At the meeting, however, Dr. Williamson reminded me that the process must fail because, according to Stenhouse, such nitrogenous matters in contact with charcoal become oxidised to nitrous or nitric acids, which of course would entirely vitiate the results.

The only foundation that I can find for this rather general opinion amongst chemists of the action of charcoal on nitrogenous organic matter, is in a lecture by Dr. Stenhouse at the Royal Institution, March 2nd, 1855. He tested some charcoal powder, which was sent to him by Mr. Turnbull, of Glasgow, and which had been closely in contact with the decaying bodies of two dogs; and he found therein "very appreciable quantities of nitric acid." He therefore describes the action of charcoal as that of a powerful oxidizer, and states "that it hastens instead of retarding the decay of putrifying substances."

This view seems to have been generally admitted as correct; but notwithstanding the eminence of the authority, I venture to call it in question, and submit that it is based on insufficient evidence. As far I am aware, the subject has not hitherto been brought to the test of actual quantitative experiments.

On March 1st, 1870, I made three mixtures with charcoal of meat, urine and excreta; and after two months keeping in loosely covered bottles exposed to the air, each mixture was tested monthly for nitrogen for six months, during which time no appreciable loss of nitrogen could be detected; nor could any trace of nitric acid be discovered in any of the mixtures. The results were communicated to the Chemical Section of the British Association at the Liverpool meeting, and published in the Chemical News, vol. xxii, page 183.

I did not anticipate any loss of nitrogen in the urine and excreta, both being partially oxidised substances, but the result with the meat was so opposed to the general view, that I determined to carry out further experiments extending over a larger space of time.

Three typical charcoals were selected, those obtained from wood, seaweed, and bone, the former a purely vegetable charcoal, the latter a purely animal charcoal, and that from seaweed one of intermediate composition,* the series representing in the order stated a diminishing proportion of carbon.

The proportion of carbon, ash, and water in each was as follows :—

	Wood.	Seaweed.	Bone.
Water	6 2	2 6	3 0
Carbon..........	92·0	63 0	9·2
Ash	1·8	34·4	87·8
	100·0	100·0	100·0
Each contained of Nitrogen..	0·20	0·92	0·50

Three mixtures were made with lean beef chopped in small pieces and then thoroughly rubbed up with the charcoal.

No. 1 consisted of wood charcoal and meat: 1000 grains of each.

No. 2 consisted of seaweed charcoal and meat: 500 grains of each.

No. 3 consisted of bone charcoal and meat: 1000 grains of each.

These mixtures were made on the 14th September, 1870, and weighed again the next day.

Each mixture was left in a loosely covered wide-mouthed bottle, freely exposed to the air, and tested occasionally for nitrogen and nitric acid.

The following tables show the analyses, extending over a period of nearly 21 months. The drying action of the charcoal is apparent from the loss of weight of the mixtures in 24 hours, amounting to 4·5 per

* It is worthy of remark that this charcoal from a vegetable so near the animal kingdom has no resemblance to that from wood, but is more like that from bone, from which it differs in containing more carbon and carbonates of calcium and magnesium, and less of phosphates of these bases.

cent. in No. 1, 7·2 per cent. in No. 2, and 3·6 per cent. in No. 3. As a rule, 50 grains were used in each experiment, 25 grains for the estimation of nitrogen, and 25 grains for testing for nitric and nitrous acids. During the whole experiment not a trace of either of these could be detected. In the estimation of nitrogen two great difficulties were encountered, and these have rendered the results very irregular, but I prefer to publish the numbers exactly as they were obtained.

Owing to the fibrous nature of the meat, great difficulty was experienced in securing average samples for analysis, and as one of the objects of the experiment was to ascertain the loss of nitrogen during the spontaneous drying of the mixtures, these were not at first artificially dried. After the first four experiments, however, that is after three months without loss of nitrogen, each mixture was dried at 212° F., but there was still difficulty in securing accurate average samples, as it was found quite impossible to dry the mixtures completely at 212° F., and it was deemed prejudicial to employ a higher temperature. Each mixture was exposed in the water-bath for 100 hours before testing. The mixtures generally absorbed at least 10 per cent. of water, and often much more from the atmosphere. The alternate absorption and drying of each mixture eight times during eighteen months, would appear to favour the oxidation of the nitrogen considerably. Moreover, the animal charcoal contains a small proportion of carbonate of calcium, and the seaweed charcoal contains 25 per cent. of this body, and a little free lime; the presence of these salts has been held as highly favourable to the formation of nitrates in the presence of organic nitrogenous matter.

No loss of nitrogen is shown in any of the mixtures at the fourth analysis, when each had lost about 40 per cent. moisture by evaporation, and had been kept three months.

It is remarkable that the two charcoals from wood and bone show little or no difference in their action, although one contains 92 per cent. and the other 9 per cent. of carbon. This alone would appear to show that the carbon acts merely as a drying agent.

If the carbon has the property generally attributed to it, we ought to find a very marked difference in the action of these two charcoals on organic nitrogenous matters. The proportion of carbon used in these experiments is double the amount necessary to preserve the meat. I do not publish these experiments as conclusive, because I believe that they do indicate a slight loss of nitrogen, but that it is much less than is generally supposed, and that it is eliminated in the form of ammonia. I have obtained satisfactory evidence of this, and hope to give further experiments in another paper.

It is however so small, that I have seen hundreds of tons of fish-offal mixed with charcoal and stored six months without perceiving

the odour of ammonia in a close shed. I have kept a mixture of evaporated urine and charcoal for several months, which yielded on analysis 22·4 per cent. of nitrogen, but of this only 10·7 per cent. came over at a red heat without soda-lime. In the following analyses soda-lime was used, but the whole of the nitrogen comes over as ammonia by simply reburning the charcoal.

The great practical importance of the question here treated induces me to bring the subject in a somewhat incomplete form before the Chemical Society, but I feel justified in drawing the following conclusions:—

1st. Charcoal mixed in equal weights with nitrogenous organic matter acts simply as a drier.

2nd. It does not act as an oxidising agent when thus applied, and does not conduce to the formation of nitrates.

3rd. It is probable that after the lapse of some time, and if the mixture be artificially dried, a small proportion of nitrogen may be eliminated in the form of ammonia.

4th. That for all practical, manufacturing, or manurial purposes, there is but little loss of nitrogen in such mixtures.

No. 1. Wood Charcoal.

1,000 *grains and* 1,000 *grains of Lean Meat, mixed September* 14, 1870:

Date.	Weight in grains.	Used in grains.	Nitrogen per cent.	Nitrogen in weight.	Nitrogen in used.	Total Nitrogen.
1870.						
1. Sept. 15	1910·0	25	1·78	33·97	—	33·97
2. Oct. 3	1351·9	50	2·15	29·06	·44	29·50
3. „ 27	1262·0	25	2·52	31·80	1 51	33·31
4. Nov. 21	1234·8	50	2·30	28·40	2·14	30·54
5. Dec 14	1099·4	25	2·80	30·78	3·29	34·07
1871.						
6. Jan. 19	1059·2	50	2·50	26·48	4·54	31·02
7. Feb. 15	1007·7	50	2·88	29·02	5·98	35·00
8. Mar. 17	952·8	50	2·88	27·44	7·42	34·86
9. June 15	905·0	50	2·28	20·63	8·56	29·19
10. Sept. 20	860·0	50	1·80	15·48	9·46	24·94
11. Dec. 30	817·4	50	1·45	11·85	10·36	22·21
1872.						
12. June 6	763·5	—	2·48	18·93	11·60	30·53

No. 2. Seaweed Charcoal.

500 grains and 500 grains of Lean Meat, mixed September 14, 1870.

Date.	Weight in grains.	Used in grains.	Nitrogen per cent.	Nitrogen in weight.	Nitrogen in used.	Total Nitrogen.
1870.						
1. Sept. 15	928·0	25	2·43	22·55	—	22·55
2. Oct. 3	680·4	25	2·88	19·60	·61	20·21
3. „ 27	648·3	25	2·99	19·40	1·33	20·73
4. Nov. 21	618·6	50	3·64	22·51	2·08	24·59
5. Dec. 14	523·6	75	3·73	19·53	3·90	23·43
1871.						
6. Jan. 19	437·5	50	3·71	16·23	6·69	22·92
7. Feb. 15	384·5	50	3·21	12·34	8·54	20·88
8. Mar. 16	330·5	50	3·46	11·43	10·14	21·57
9. June 15	283·5	50	3·01	8·53	11·87	20·40
10. Sept. 20	232·0	50	3·35	7·77	13·54	21·31
11. Dec. 30	201·0	50	2·10	4·22	15·21	19·43
1872.						
12. June 5	161·6	—	3·55	5·73	16·98	22·71

No. 3. Bone Charcoal.

1,000 *grains and* 1,000 *grains of Lean Meat, mixed September* 14, 1870.

Date.	Weight in grains.	Used in grains.	Nitrogen per cent.	Nitrogen in weight.	Nitrogen in used.	Total Nitrogen.
1870.						
1. Sept. 15	1926·4	25	1·88	36·21	—	36·21
2. Oct. 3	1390·7	50	2·25	31·29	·47	31·76
3. „ 27	1258·5	25	2·47	31·08	1·59	32·67
4. Nov. 21	1232·0	50	3·10	38·19	2·21	40·40
5. Dec. 14	1105·4	25	3·18	35·15	3·76	38·91
1871.						
6. Jan. 19	1065·2	50	2·85	30·35	5·18	35·53
7. Feb. 15	1001·0	50	3·13	31·33	6·74	38·07
8. Mar. 16	955·0	50	3·41	32·55	8·44	40·99
9. June 15	900·5	50	2·38	21·55	9·63	31·18
10. Sept. 20	855·5	50	3·51	30·02	11·38	41·40
11. Dec. 30	812·7	50	1·27	10·32	13·13	23·45
1872.						
12. June 6	738·5	—	2·68	19·79	14·47	34·26

IV.—*On Iona Pebbles*

By Edw. C. C. Stanford, F.C.S.

Analysis of Iona Pebbles.

	Light.	Dark.
Silica	37·20	43 20
Lime	5·03	5·10
Magnesia	36 73	33·60
Ferrous oxide	5 39	6·00
Manganese oxide ..	4·19	·94
Water............	11·42	9 60
	99·96	98·44

Tourists visiting the island of Iona have some difficulty in leaving without purchasing small. water-worn, translucent pebbles, of a peculiar light olive-green colour. These are found on the shores of this island and the island of Tyree: the specimens accompanying this paper are from the latter island. The mineral is a variety of non-aluminous serpentine, and is peculiar from its containing manganese as a constituent. Except in Iona, this mineral and the remarkable pink marble (described in a paper published in the *Chemical News*, vol. 22, p. 171), are not, I believe, found elsewhere.

V.—*On Anthraflavic Acid.*

By W. H. Perkin, F.R.S.

About twelve months since I brought before the Society an account of this substance, which is a secondary product of the manufacture of alizarin, and was first observed by Dr. Schunck, who examined it and gave it the name of anthraflavic acid. It will be remembered that the conclusion I arrived at was that it was an isomeride of alizarin, or in other words, a dioxyanthraquinone. This has since been confirmed by Herr Auerbach.

I have lately been engaged with further experiments on this body, and in preparing some of its derivatives, and I now beg to lay before the Society an account of my results.

Anthraflavic Acid.

It is known that when strongly heated, anthraflavic acid gives a sublimate of golden-yellow crystals in the form of leaves or plates, a

certain amount being at the same time carbonized. This sublimate has all the properties of the acid; but as its composition had not been fixed by analysis, it appeared to me desirable to submit it to further examination. For this purpose a quantity of the perfectly pure acid was sublimed, and the sublimate crystallised from alcohol; in this manner it was obtained in yellow, silky needles. A specimen dried at 190° C. gave the following numbers:—

·1442 of substance gave
·3712 of CO_2, and
·0448 of H_2O.

These agree with those required by the formula,

$$C_{14}H_8O_4.$$

The following is a comparison of the experimental and theoretical numbers:—

	Theory		Experiment.
C_{14}........	168	70·00	70·02
H_8........	8	3·33	3·45
O_4........	64	26·67	—
	240	100·00	

Dr. Schunck mentioned that anthraflavic acid when fused with alkali, was converted into alizarin, and I was also under the same impression; but from more recent experiments I am inclined to doubt the correctness of this statement, as the colouring matter thus obtained produces an orange-red colour with alumina mordants. I hope, however, to examine this reaction carefully.

Diacetyl-anthraflavic Acid.

On heating anthraflavic acid with acetic anhydride in a sealed tube, to about 160° C., it gradually dissolves, and if the temperature be maintained for four or five hours, it will entirely disappear, but on cooling the fluid product deposits a large quantity of beautiful crystals, their colour and shape being entirely different from those of anthraflavic acid.

This product is purified by draining off the unused acetic anhydride, and recrystallising once or twice from glacial acetic acid; it is then obtained in beautiful, very pale, yellow crystals, not unlike benzoic acid in shape, but small. Two specimens dried at 150°—160° C., gave on analysis the following numbers:—

I. ·2818 of substance gave—
·6888 of CO_2, and
·0932 of H_2O.

II. ·2515 of substance gave—
·6137 of CO_2, and
·0848 of H_2O.

These numbers give percentages agreeing closely with the formula

$$C_{14}H_6O_2\left\{\begin{matrix}(C_2H_3O)O\\(C_2H_3O)O\end{matrix}\right. = C_{18}H_{12}O_6$$

as the following comparisons will show:—

	Theory.		Experiment. I.	Experiment. II.
C_{18}	216	66·66	66·66	66·55
H_{12}	12	3·70	3·67	3·74
O_6........	96	29·64		
	324	100·00		

This substance is therefore *diacetyl-anthraflavic acid.* It melts at 228°—229° C., and may be volatilized with but little decomposition. It is difficultly soluble in alcohol, but moderately so in boiling glacial acetic acid. Alcoholic potash decomposes it, regenerating anthraflavic acid. It dissolves in concentrated sulphuric acid, with an orange-red colour; water throws down from this solution a yellow precipitate, apparently anthraflavic acid.

Diacetyl-alizarin.

As the acetylic derivative of alizarin is isomeric with the body just described, I was desirous of comparing the two substances. To prepare diacetyl-alizarin, I heated some alizarin from anthracene in a sealed tube to 160° C., for a few hours with acetic anhydride. On cooling, the product, which had partly separated as a yellow crystalline substance, was heated with water to remove the remaining acetic anhydride, then collected on a filter and dried. After being crystallised two or three times from alcohol, it was obtained as a pale yellow substance, crsytallising in flat needles or plates. A specimen dried by fusion gave on analysis the following numbers:—

·4190 of substance gave
1·0037 of CO_2, and
·139 of H_2O.

These numbers give percentages agreeing closely with those required by the formula of diacetyl-alizarin,

$$C_{18}H_{12}O_4$$

	Theory.	Experiment.
Carbon	66·66	66·35
Hydrogen	3·70	3·68

These results correspond with those obtained by Hr. Schrödter (*Ber. Deut. Chem. Ges.*, Berlin, No. 16, p. 870).

Diacetylalizarin, when heated with alcoholic potash, rapidly decomposes with formation of potassic alizarate. It differs from diaceto-anthraflavic acid by being much more soluble in alcohol and glacial acetic acid, and by fusing at 68° lower, or at about 160° C.

Dibenzoyl-anthraflavic Acid.

When anthraflavic acid is boiled with an excess of chloride of benzoyl, it soon dissolves, hydrochloric acid being evolved in abundance. After the ebullition has been continued for a few minutes, the liquid is quite clear. On slowly cooling, however, it becomes filled with needle-shaped crystals, like anthraquinone. These can be rendered pure by repeated washings with glacial acetic acid, and then with alcohol. This substance is of a pale yellow colour; it gave on analysis the following numbers :—

I. ·2824 of substance gave
·7751 of CO_2, and
·092 of H_2O.
II. ·2955 of substance gave
·8117 of CO_2, and
·0965 of H_2O.

These gave percentages agreeing with the formula

$$C_{14}H_6O_2\left\{\begin{matrix}(C_7H_5O)O\\(C_7H_5O)O\end{matrix}\right. = C_{28}H_{16}O_6,$$

as the following comparison will show :—

	Theory.		Experiment.	
			I.	II.
C_{28}	336	75·00	74·85	74·91
H_{16}	16	8·57	3·61	3·62
O_6	96	21·43	—	—
	448	100·00		

Dibenzoyl-anthraflavic acid melts at 275° C. It is insoluble or nearly so in alcohol; boiling glacial acetic acid dissolves it in minute quantities only, and deposits it on cooling in very fine needles. It is but slowly acted upon by alcoholic potash. With concentrated sulphuric acid

it behaves like the acetyl-derivatives, but dissolves with more difficulty. In the last number of the *Berichte der Deutschen Chemischen Gesellschaft*, 1872, No. 16, Berlin, Liebermann has published a paper on "Monoxyanthraquinone and Anthraflavic Acid." In this he refers to his former paper, "On a By-product in the Manufacture of Alizarin;" in which, it will be remembered, he describes a yellow crystalline compound. From its origin and properties it appeared to be the same substance as anthraflavic acid, but from his analysis he viewed it as monoxyanthraquinone. The fresh examination of this substance has confirmed the correctness of his formula, $C_{14}H_8O_3$. The remarkable point, however, consists in the fact that Herr Auerbach obtained anthraflavic acid from a similar material to that used by Liebermann. This would appear to show that both substances are produced in the manufacture of alizarin, and are separated in its purification, the different results obtained by Liebermann and myself being due to the different modes of working. Liebermann's oxyanthraquinone appears to be easily soluble in cold baryta-water, whilst anthraflavic acid is nearly insoluble; therefore, as the method employed by me for obtaining anthraflavic acid in a pure state consisted in recrystallising the barium salt, it is certain that the more soluble barium compound of oxyanthraquinone, if present, would be left in the mother-liquor.

I have but little doubt that had Liebermann employed the method described for the preparation of anthraflavic acid, he would have had no difficulty in obtaining it. It is, however, of considerable interest to know that both substances exist.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Chemical Efficiency of Sunlight. By JAMES DEWAR. (Phil. Mag. [4], xliv., 307–311.)

THE author endeavours to calculate, in dynamical measure, the chemical efficiency of sunlight from statistics as to growth of green foliage, and from the known action of sunlight upon it.

Under the influence of light, carbonic anhydride and water are split up by the action of the chlorophyll of the leaf. The carbon and hydrogen of the two bodies are absorbed or assimilated by the plant, and part of the oxygen is given off into the air. Mr. Dewar, on the authority of Boussingault, represents the reaction that takes place as follows:—

$$CO_2 + H_2O = COH_2 + O_2.$$

The body COH_2 is taken up by the plant, and, subsequently or simultaneously, is converted in the following way:—

$$6(COH_2) = C_6H_{12}O_6.$$

Thus the glucose form is obtained which, more or less modified, is the basis of ordinary organisms.

Recent observations of Boussingault have shown that, under favourable circumstances, one square decimeter of green leaf decomposes, as a mean, 5·28 cubic centimeters of carbonic acid gas per hour. Now, from determinations made by Frankland, Mr. Dewar calculates that the complete change of 1 cent. cub. of carbonic acid gas into grape-sugar requires 4·78 gram-units of heat. Hence $5·28 \times 4·78 = 25·23$ represents, in gram-units of heat, the energy absorbed per hour by one square decimeter of green leaf exposed to sunlight. An estimate of Pouillet gives for the mean total solar radiation per hour per square decimeter exposed perpendicularly to the sun's rays at Paris, 6,000 gram-units of heat. Hence $25·23 \div 6,000$, or $\frac{1}{238}$, is a fraction which represents the quantity of the total energy obtainable from the sun that is stored up for us by the action of the earth's vegetation.

There is little doubt, it appears, that this number is not too great; in fact, circumstances might occur under which a much larger fraction of the radiated energy might be stored up.

It is to be considered, however, that any alteration in the solar rays that fall upon the green leaf surface (alterations such as might be caused by changes in the absorptive powers of the earth's atmosphere), might produce changes in the rate of decomposition by the leaf surface, and in fact may cause the water and carbonic acid to be attacked in a proportion different from that which is represented by the chemical equation given above. This would cause the same plant under different atmospheric conditions to form and assimilate various substances.

J. T. B.

Analysis of the Light emitted by Phosphorescent Uranium Compounds. By E. BECQUEREL (Compt. rend., lxxv., 296–303).

THE author employs two methods of observation. The salt to be examined is placed in a phosphoroscope, the moveable disc of which, having four openings, rotates 300 times in a second; the solid is illuminated by sunlight reflected from a heliostat and concentrated by a lens. The light which the substance emits is analysed by a spectroscope. This method answers very well for those solids which continue phosphorescent for the time necessary for the disc to pass through one quarter of its revolution, but for some of the compounds it does not answer so well. The second method is to illuminate the substance or solution with the light of the more refrangible end of the spectrum, from the blue to violet, for the phosphorescent light is always less refrangible than the incident light. A solution of ammoniacal cupric sulphate acts as a good medium for cutting off all the red end of the spectrum. The phosphorescent light from the substance is concentrated by a lens and analysed as before. Experimenting in this way, the author finds that the uranous compounds do not show any appreciable effect of phosphorescence, but that the greater number of the uranic or uranyl compounds are more or less strongly phosphorescent. These compounds generally give a series of almost equidistant groups of luminous and dark bands reaching from C to F; these groups generally number 5, 6, or 7, but do not occupy precisely the same positions in the spectra of different compounds.

If this succession of the groups of lines characterises the compounds of uranium, the acid in combination determines the disposal of the luminous and dark bands of each group. In the double salts of the same class, as in the sulphates and double sulphates, the detail of each group remains the same, but the index of refraction of the corresponding groups is altered, sometimes on the side of greater and sometimes on the side of less refrangibility. When the solid compounds of uranium are illuminated by transmitted violet light, groups of absorptive bands in the most refrangible part of the spectrum are seen, which are different in each compound, and appear to correspond to the less refrangible groups of bright bands of phosphorescence, and to be a continuation of them. A. P.

Effect of surrounding the Negative Electrode of a Carbon-battery with Charcoal Powder. By TH. DU MONCEL (Compt. rend., lxxv., 876–879).

AN effect analogous to that which is produced by platinising the platinum-plate in Smee's battery, can be obtained by surrounding the negative electrode of a carbon-battery with coarsely-powdered charcoal. Different kinds of carbon, with different electro-motive forces, were found to exhibit the same kind of polarity towards each other, whether they were opposed to each other in plates or cylinders, or in the state of powder. By the addition of a little water, two intimate mixtures were made, one of the powder of the two most electro-positive, and

another of that of the two most electro-negative carbons, which were at the disposal of the author. Two carbon cylinders, A and B, were now taken, and after it had been determined that the two, when placed beside each other in water, produced a deflection of about 25° to 30°, and that A was positive towards B, the carbon A was placed within a porous vessel filled with the positive mixture. As soon as this vessel was immersed in water beside B, the galvanometer indicated a change in the direction of the current lasting about a quarter of an hour, after which time the current resumed its original direction, and increased in the course of an hour and a quarter so much as to produce a deflection of 84°. The effect of the mixture was accordingly at first to reverse the positive polarity of A, and afterwards to augment it very considerably and durably.

The carbon A was now removed from the mixture, well-washed, and placed beside B as before, without intervening cell. The current produced a deflection of 51 , showing that the carbon had gained in electromotive force by the temporary contact with the mixture. When now the carbon B was placed in the porous cell containing the positive mixture, the galvanometer indicated during the first quarter of an hour a current flowing from B and A; after this time the deflection changed to the other side, and increased, after five quarters of an hour, to 73° in the normal direction. On removing B from the mixture, and placing it beside A as before, a current was at first obtained almost as strong as when the mixture was there; but it abated gradually, and after twenty minutes caused a deflection of only 49° in the normal direction.

The effects of the negative mixture on the carbons are similar, but not quite so strong as those of the positive mixture.

These experiments prove (1) that a carbon mixture, during the first quarter of an hour, reverses the polarity of a positive, and increases that of a negative carbon; and (2) that, after this time, the first effect is reversed, inasmuch as an originally negative carbon becomes strongly positive, and an originally positive carbon becomes *more* positive than before.

Since the charcoal powder acts as it were like a conducting filter, it is best to employ it in the state of coarse powder, which offers less electrical resistance than fine powder. It is probable that the advantage of the charcoal powder is at least partly due to its increasing the surface of the negative carbon.

R. S.

On the Application of Electrolysis to the Determination of Molecular Weights. By A. Ladenburg (Deut. Chem. Ges. Ber., v, 753.)

This is a criticism of Paternò's paper on the same subject (*Gazzetta Chimica Italiana*, ii, 245), in which the conclusion deduced by that chemist, that *an electric current passing through a number of electrolytes, decomposes in each of them the same number of molecules*, is shown to be erroneous, by considerations similar to those already adduced in this Journal (p. 1070 of last volume).

Ladenburg further points out that the idea of equivalent plays a very important part in the chemistry of the present day, and is by no means superseded by that of molecule. "Modern chemistry" is founded indeed on the separation of these two ideas, and the molecular weight of a compound can no more be determined by the results of its electrolysis than by the formation of neutral salts. If for example the same electric current separates equal quantities of silver from the sulphate and the nitrate of that metal, this result can no more be regarded as demonstrating the correctness of the molecular formulæ Ag_2SO_4 and $Ag_2N_2O_6$, than the known fact that the same quantity of silver oxide is dissolved and converted into neutral salts, by quantities of sulphuric and nitric acid represented by the formulæ H_2SO_4 and $H_2N_2O_6$.

H. W.

Water in Electrolyses is not decomposed by the Current.

By E. Bourgoin (Bull. Soc. Chim. [2], xvii, 244).

This paper describes the results of experiments on the electrolysis of aqueous acids, in a vessel divided into two equal parts by an impervious diaphragm, pierced with an aperture of such a size as to allow the passage of the current, but absolutely to prevent the mixture of the liquids in the two compartments. The apparatus is so disposed that the gases evolved at the two poles may be collected separately, and when the experiment is terminated, the two compartments are separated, and the liquid in each is analysed.

Supposing now the liquid electrolysed to be water acidulated with *sulphuric acid*, and the hydrogen to be collected. Let its weight be denoted by P. It is then observed—and this is the main point of the result—that the acid in the positive compartment is increased by a certain quantity α, while that in the negative compartment has diminished by exactly the same amount: the quantity of sulphuric acid electrolysed is therefore equal to 2α; and this quantity corresponds to a proportion of hydrogen denoted by $\frac{P}{3}$. Hence it follows that the compound electrolysed is not SO_3H_2O but $(SO_3H_2O + 2H_2O)$.

This result can be explained on two hypotheses only:—

1. The water and the acid are decomposed by the current in succession:—

$$SO_3H_2O = (SO_3 + O) + \ldots\ldots\ldots\ H_2$$

Positive pole. Negative pole.

$$2H_2O = O_2 + \ldots\ldots\ldots\ 2H_2$$

2. The current decomposes a body represented by the formula, SO_33H_2O:—

$$SO_33H_2O = (SO_3 + O_3) + \ldots\ldots\ldots\ 3H_2.$$

That the latter interpretation is the only one admissible, seems to follow from the fact that when currents of different intensity are made to pass through aqueous sulphuric acid of various degrees of concen-

tration, comprised between the limits $SO_3 3H_2O + 3$ aq., and $SO_3 3H_2O + 125$ aq, the preceding ratio is found to hold good in all cases, which could scarcely be the case if the water and acid were electrolysed independently. Still this fact cannot be considered quite conclusive, although the existence of the hydrate $SO_3.3H_2O$, or $SO_4H_2 2H_2O$, is not altogether hypothetical, having indeed been deduced from the phenomena of maximum contraction observed to take place when two molecules of water, H_2O, are added to a molecule of sulphuric acid, SO_3H_2O.

In the case of aqueous *nitric acid*, the decomposing action of the current is exerted exclusively on the group $N_2O_5 4H_2O$ [or $2NO_3H_3.H_2O$], the existence of which is generally admitted, though it does not crystallise. The decomposition is—

$$N_2O_5.4H_2O = (N_2O_5 + 2O_2) + \ldots\ldots\ldots\ 4H_2.$$

In the case of *oxalic acid*, the action of the current is exerted exclusively on the group $C_2H_2O_4 2H_2O$, which is well known to exist as a crystalline hydrate—

$$C_2H_2O_4.2H_2O = (C_2O_4 + O_2) + \ldots\ldots\ldots\ 3H_2.$$

As, however, nothing but carbon dioxide is evolved at the positive pole, it must be inferred that the oxygen decomposes a corresponding quantity of oxalic acid, according to the equation—

$$2C_2H_2O_4 + O_2 = 4CO_2 + 2H_2O.$$

It follows, then, if this interpretation is correct, that the loss of acid at the positive pole should be greater than at the negative; and in fact experiment shows that the quantities of acid thus lost at the two poles are to one another as 3 : 1, which is in exact accordance with the preceding equation:—

Oxalic acid decomposed	at the pole N	by the current ..	1 molecule
	at the pole P	by the current ..	1 "
		by the oxygen ..	2 "

Again, when aqueous *formic acid* is submitted to electrolysis, nothing but carbon dioxide is evolved during the whole of the reaction, a fact which can be explained only upon three hypotheses, viz.:—

1. The current acts solely on the acid:

$$2CH_2O_2 = (C_2H_2O_3 + O) + \ldots\ldots\ldots\ H_2,$$

at the positive pole:

$$2(C_2H_2O_3 + O) = 2CO_2 + 2CH_2O_2.$$

2. The water alone is decomposed:

$$2CH_2O_2 + O_2 = 2CO_2 + 2H_2O.$$

3. The water and acid are decomposed simultaneously:

$$2(C_2H_2O_3O) + O_2 = 4CO_2 + 2H_2O.$$

Now let α be the quantity of formic acid decomposed by the current: then, in the first case, the loss of acid is nothing at the positive, and equal to $\frac{\alpha}{2}$ at the negative pole; in the second case, on the contrary, it is nothing at the negative, and equal to α at the positive pole; and in the third, it is equal to $\frac{\alpha}{2}$ at both.

Now experiment shows that there is *no loss of acid* at the positive pole: consequently the water has not been decomposed by the current.

Exactly similar results are obtained when alkalis or salts are dissolved in the water instead of acids.

The conclusion of the whole is that *water is not an electrolyte.**

H. W.

Active Properties acquired by some Gases under the Influence of the Silent Discharge of Electricity. By M. CHALERIER (Compt. rend., lxxv, 536—539).

A CURRENT of hydrogen, which in a Houzeau's ozonising tube had been exposed to the silent electric discharge, was passed over silver oxide in a small, thimble-shaped glass vessel, which was closed by a cork with two tubes. Silver oxide, which after its preparation had been allowed to stand for about a month, underwent on exposure to the electrified hydrogen no change appreciable either by the microscope or by the balance. But when silver oxide, freshly prepared and still retaining some of its moisture, was acted upon, its surface began to blacken, and became studded with shining particles of metallic silver, between which splinters of glass, similar to those described by Thénard, could be distinguished. The metallic particles when exposed to the air, appeared to change their form, leaving behind a small crystalline skeleton.

When silver thus partially reduced was again submitted to the action of electrified hydrogen, and then examined under the microscope, minute, extremely thin coils of metallic silver, were seen to project from the surface, as if they had, whilst in a semifluid state, been pressed out from the layer of silver oxide. The author concludes from this, that freshly reduced silver forms a compound with hydrogen, which is fluid, very unstable, and exhibits the phenomenon of "spitting" when the absorbed gas escapes.

A perfectly smooth, thin, circular disc of pure silver, exposed for several hours to the action of electrified hydrogen, did not appear to

* This conclusion is most probably right, being supported by other considerations (see p. 1070 of last volume); but the author's experiments can scarcely be regarded as affording fresh evidence in support of it. In fact they seem to be explicable on the hypothesis of the electrolysis of water (with secondary action of liberated oxygen) accompanied by migration of the elements of the electrolytes present: the result of the first experiment, for example, may be explained by supposing that while a weight P of hydrogen is disengaged by decomposition of water, a weight $\frac{\alpha}{2}$ of the liquid passes through the diaphragm without decomposition. The assumption that an aperture can be made of sufficient size to give passage to the current, and yet so small as absolutely to prevent the mixing of the liquids, is inadmissible.—H. W.

undergo any change; but on the admission of air it became covered with a whitish film, which under the microscope resembled silvered shagreen. A slight swelling was visible round the edges of the disc, from which minute pieces of silver could be detached, looking as if they had just been melted. These results prove that hydrogen retains for a little time, and at a short distance from the electrifying tube, the active properties imparted to it by the silent discharge.

R. S.

Determination of Melting-points. By E. KOPP (Deut. Chem. Ges. Ber. v., 645).

INSTEAD of using an oil-bath or sulphuric acid, it is more convenient to use a mercury-bath. The substance is placed on the mercury and covered with a small funnel of thin glass. The melting point and the point of solidifying can be observed most readily if the substance is opaque, and becomes transparent on fusion. If a substance is softened before melting, it is fused and introduced in a little conical capillary tube, which, after cooling, is placed 0·5 — 1 centim. below the surface of the mercury. As soon as the substance becomes soft, or begins to melt, it is forced out of the tube, and appears above the surface of the mercury.

C. S.

On the Various Vibratory Motions produced by Detonants. By P. CHAMPION and H. PELLET (Compt. rend., lxxv, 712–715).

THE authors have made further experiments on the subject lately investigated by them, and described in a previous communication (*Compt. rend.*, lxxv., p. 110, and *Chem. Soc. J.*, 1872, pp. 187, 874). Their object is to find out what is the difference between the vibratory motions excited by various detonants, and thus to account for the difference in their powers of causing, by means of the intermediate air, the explosion of other detonants placed at a distance.

They arranged a series of sensitive flames corresponding to the complete scale of *g* major, precautions being taken to tune the flames exactly to the proper pitch. Small quantities of various detonants were then exploded at a distance of 5 meters from the flames. In the case of iodide of nitrogen and mercuric fulminate, 0·03 gr. of each being exploded, the former produced no effect upon the flames, while excitement of the flames *a*, *c*, *e*, *f*, *g*, was noticed on the explosion of the latter. This appears to show that the vibrations excited by the two explosions are very different, and also that the vibrations excited by mercuric fulminate act on the flames belonging to some notes of the scale to the exclusion of others.

Secondly, exploding these bodies at a shorter distance from the flames, they found that, while the iodide of nitrogen affected the higher notes of the scale, and those only, the mercuric fulminate acted on all the flames.

Two-tenths of a grain of iodide of nitrogen, placed at a short distance from the flames, was found to influence them all.

The above experiments seem also to indicate, from the difference observed with the same amount of the same detonant placed at different distances, that acute sounds predominate in explosions.

Nitroglycerin gave no results with the analysing apparatus when compared with mercuric fulminate. The same may be said of nitroglycol, nitroerythrite, and nitrodulcite. It is probable that this was due to the small range of the apparatus, and that on constructing a set of flames graver than those used during these experiments, the upper sounds of the explosions due to these bodies might have been reached.

J. T. B.

Researches on Crystalline Dissociation.—Estimation and Distribution of the Force in Saline Solutions. By P. A. FAVRE and C. A. VALSON (Compt. rend., lxxv, 330—336, and 385—388).

IT is evident, from the generally admitted principle that the different forces necessary to produce a given effect are equivalent, that the contractions produced in the liquid: (1) by lowering the temperature; (2) by external compression; (3) by the solution of a salt, may be considered as three effects of the same order, and consequently equivalent to the forces which produce them. It may be shown from the known coefficient of the expansion of water, that the contraction of 1 c. c. per litre at 15°, is equivalent to a depression of temperature of 7·576°, or 7576 heat-equivalents; moreover, a similar contraction would be produced by an external pressure of 21·34 atmospheres. From this, it may be inferred, that if a litre of water at 15° be subjected to a compression of 21·34 atmospheres, it would disengage 7576 heat-equivalents. The authors are having apparatus constructed for investigating this question.

An equivalent of carbonic anhydride, in passing from the gaseous to the solid state, disengages 3058 heat-equivalents, but when condensed in the pores of charcoal, it disengages 3278, from which it would appear that the condensation of the gas has advanced a degree beyond that of solidification; and since the disengagement of heat is greater at the commencement of the action, we may consider that each molecule of carbon is the centre of action, about which are grouped layers of carbonic anhydride, more and more condensed as they are nearer the centre. In a similar manner, in a solution of salt, such as crystallised sodium sulphate, we may regard the aqueous molecules as grouped about the saline molecules like the layers of carbonic anhydride round the carbon molecule, a supposition supported by the raising of the boiling point, the lowering of the freezing point, and the diminution of the vapour tension of the solution.

The authors find, as the results of their experiments, that anhydrous sodium sulphate in combining with 10 equiv. of water, to form crystalline sodium sulphate, undergoes a total contraction of volume from 116·5 c.c. to 110·0 c.c., which measured in heat-equivalents is 49244; also 1 equivalent of anhydrous salt (71 grms.), dissolved in a litre of water, causes a contraction of 16·7 c.c., measured by 126519 heat-equivalents, and the crystallised salt (161 grms.), 10·5 c.c., measured by 79548 heat-equivalents, whilst the numbers obtained for the two

latter, by actual observation of the calorimeter, are + 354 and − 9300 respectively, representing the difference in heat-equivalents between the contrary thermic effects corresponding to the contraction of volume, and that of the interior force of association between the salt and the water. When a salt is dissolved in water, the heat rendered disposable by the contraction of the water, is absorbed, partly in reducing the solid body to a liquid state, and partly by the reaction between the salt and the solvent.

On comparing the results obtained (*Compt. rend.*, 17th August, 1871), in the estimation of the densities of saline solutions, it will be observed that each saline radical produces a contraction of volume in the solvent peculiar to that radical, so that each radical absorbs from the solvent an amount of heat which is always the same, and which remains independent of the other radical with which it is associated.

C. E. G.

Researches on Crystalline Dissociation. The Alums. By P. A. FAVRE and C. A. VALSON (Compt. rend., lxxv, 925—930 and 1000—1005).

As water dissolves out the potassium sulphate from calcined chromo-potassic alum, leaving chromium sulphate, it would seem that water effects the dissociation of the saline constituents of the alum, although heat does not. From the tabulated results of observations of the densities of the alums, the authors conclude that the molecular volumes of the crystallised alums are sensibly the same, so that they may be regarded as crystalline edifices composed of an equal number of molecular layers, of which the structure and dimensions are sensibly the same. They also observe that the total contraction which takes place in the union of the anhydrous salts with water to form the crystal, is greater than that caused by the solution of the latter. This is the inverse of what takes place with sodium sulphate, the difference being produced by the influence of the crystalline form on the phenomenon of contraction. When solutions of the violet chrome-alums are heated in closed vessels, they become green and diminish in density, showing that the coercive action is less in the case of these transformed alums. For alums, as for solutions of other salts, each substitution of a molecule of a base for another isomorphous with it, causes a variation in the density and capillary height of the solution, depending solely on the nature of the molecule, and independent of the actions of the same order exercised by the other molecules present.

There are tables appended of the modulus of the capillarity and of the density of the alums, and also of the density and capillarity calculated from them, as compared with those obtained by actual observation, which agree very closely. These thermic experiments have established, as a fact, that the double salts, and especially the alums, are resolved into their constituent salts in the presence of water, a result which is, moreover, confirmed by the experiments on the modulus of capillarity and of density.

A comparison of the tabulated results contained in this and the previous communication (*Compt. rend.*, lxxv, 801; *Chem. Soc. J.*, 1872,

1068), shows that the different salts, such as the ammonium, potassium, and aluminium sulphates, produce very different variations, during solution, not only in volume but also in the thermic effects as exhibited by the calorimeter. The authors infer from this, that a relation exists between the thermic effects and the effects of contraction which accompany the solution of salts, a view confirmed by the phenomena observed during the solution of the partially dehydrated and the hydrated alums. In fact, when the crystalline aluminium and chrome alums are dissolved, they produce the same depression of temperature, and also a contraction of volume which is sensibly equal. It must not, however, be supposed that the exterior thermic effects exhibited by the calorimeter are always proportional to the contraction, for the phenomenon of solution is necessarily a complex one, involving the action of various forces.

Two tables accompany the memoir, the latter of which "V" gives, for the alums—1. The internal mechanical force, expressed in heat equivalents, corresponding to the coercive force of the anhydrous salt on the water in which it is dissolved. 2. The force employed in the solution of the crystallised salt. 3. The mechanical force employed in the formation of the crystal. As the numbers in this table are very high, and the difference between them and those obtained by actual calorimetrical observations is far greater than can be accounted for, either by the fusion of the water of crystallisation of the salts, or even of the salts themselves, the authors ask whether this does not point to a deeper internal modification? Are not the elements of the salt more or less dissociated by the act of solution? They believe this to be the case, and that not only does solution give the elements of the compound a reciprocal independence, but the internal mechanical force necessary to produce this effect may be measured by the change in volume which accompanies solution.

C. E. G.

Dissociation of Ammoniacal Salts and Acetates.

By H. C. Debbits (Deut. Chem. Ges. Ber., v, 820).

Fittig has shown that an aqueous solution of sal-ammoniac is decomposed by boiling, an ammoniacal distillate being formed. The author finds that hydrochloric acid is also contained in the distillate. Solutions of ammonium nitrate, sulphate, oxalate, and acetate lose ammonia, not only by boiling, but also at the ordinary temperature, and even at 0°, if a stream of pure hydrogen be passed through a saturated solution of the salt; the first three salts furnish a distillate not containing any acid: but the other salts give distillates, which are first alkaline, then neutral, and finally acid. Weaker solutions of ammonium chloride yield relatively more ammonia on distillation than stronger ones.

Solutions of the acid sulphate and oxalate, and the quadroxalate of ammonia, gave distillates containing only infinitesimal quantities of ammonia.

When a solution of ammonia or of acetic acid is distilled, a certain portion of the ammonia or acid is contained in a given quantity of distillate; by distilling the solution of an acetate or of an ammonia salt, and determining the quantity of acid or of ammonia in the distillate,

the author obtained the means of calculating the amount of dissociation which had taken place. He gives the following results:—

Sodium acetate	0·14 per cent.	at 100°—102°.
Barium "	0·064 "	at 100°—101·5°.
Lead "	5·0 "	at 100°.
Silver "	0·72 "	at 100°.
Ammonium chloride .	0·062	at 100°, the boiling point of the solution being scarcely raised on account of the small quantity of salt employed.
Nitrate............	0·072	
Sulphate	1·1	
Oxalate............	6·7	
Acetate............	7·0	

C. R. A. W.

Action of Heat on Solutions of Hydrated Salts.

By C. Tichborne (Chem. News, xxv, 133).*

The chlorides of cobalt, copper, and nickel are not separated from their water of hydration in a neutral solution, by simple boiling at the ordinary pressure. Separation takes place, however, on boiling at increased pressure, and the thermanalytic point (see *Chem. News.*, xxiv, 123), is brought below 100° C. at the ordinary pressure, if a dehydrating substance be present. Cobalt chloride gives the most striking results.

An absolute alcoholic solution of this salt is of a deep blue colour. When water is carefully poured down the side of a vessel containing such a solution, two layers of liquid are formed, the upper blue, and the lower pink. When the whole is mixed, and heat is applied to the liquid, which is now pink, it passes through all the shades of pink and purple, till a pure blue is produced, giving the absorption-spectrum of the anhydrous salt. Upon dipping the vessel at once half way into a freezing mixture, the two layers are reproduced, the lower being pink, because the decomposing action of the heat is removed, and the upper remaining blue as long as it is hot.

When a weak aqueous solution of cobalt chloride is boiled in a sealed tube, one-third filled, the colour gradually passes from pink to blue.

The blue aqueous solution of cupric chloride, when heated in a sealed tube to a high temperature, becomes gradually green, then yellow, and ultimately dark brown and nearly opaque. On cooling it regains its original appearance, except that a slight opalescence of basic salt is formed; this may, however, be prevented by adding a little acid, which also renders the liquid still more sensitive to heat.

An aqueous solution of nickel chloride heated under pressure has its green colour at first intensified; it then becomes yellow, and finally yellowish-green. This behaviour, though somewhat anomalous, indicates similar decomposing action to that in the cases of cobalt and copper. The same anomalies are observed when an absolute alcoholic solution of this salt is mixed with weaker alcohol.

* On Molecular Dissociation; see also Tichborne (Chemical News, xxiv, 123, 199, 209, 220).

The sealed tube used in some of the above experiments was $\frac{1}{50}$ inch in diameter, and was enclosed in a larger tube, as explosions sometimes took place.

B. J. G.

On the State of Salts in Solution. By M. BERTHELOT and L. DE SAINT-MARTIN (Ann. Chim. Phys. [4], xxvii, 433—462).

A NEW method for settling some of the vexed questions as to the state of salts in solution is proposed by the authors of the present paper. When a quantity of ether is shaken up with the aqueous solution of bodies (such as organic acids), which the ether itself dissolves, the water yields up to the ether a definite proportion of the body. On allowing the ether to float to the top, the quantity of the body taken up by it can be determined, and from this the quantity originally contained by the water can be inferred. This may be done in cases in which it would be difficult to determine directly the amount of the body in the aqueous solution.

The authors have applied the method—

1. To the determination of the state of acid salts in solution.
2. To the question of the division of a base between two acids in solution.

An example will explain the mode of operation. Suppose that an acid salt is partially decomposed by solution in water: there are then present together in the solution a portion of the salt in its original form as an acid salt, and also free acid and neutral salt, due to the part of the original salt broken up. It would be impossible under these circumstances to determine the quantity of the free acid in the aqueous solution. But if the acid be soluble in ether, and supposing, as a simplification, that neither the acid salt nor the neutral salt is soluble in ether, then on determining the quantity of acid taken up by a certain volume of ether, and knowing what may be called the co-efficient of division, that is the ratio in which ether takes up the acid in question from an aqueous solution of it, it is easy to determine the quantity of acid set free on dissolving the acid salt in water. The example here given is sufficient to explain the principle. The details of experiment and the devices adopted when the solutions are concentrated, in which case the co-efficient of division is not constant, but depends on the temperature, are fully described in the original paper.

The following are some of the results arrived at. Taking organic salts, such as acetates and oxalates, it appears at once that there is a vast difference between them when in solution It seems to be really possible to have in solution an acid salt of the bibasic acid, such for instance as potassium bioxalate, or potassium and hydrogen oxalate, but sodium biacetate is immediately, on solution, broken up into neutral sodium acetate and free acetic acid. On the other hand, on trying to dissolve potassium quadroxalate, it was found to break up into free oxalic acid and potassium bioxalate. Similar results were obtained with the salts of succinic acid. Experiments were also tried as to the stability of potassium bioxalate in presence of free oxalic acid, and it was found to be much increased. The influence of dilution was also

examined. The conclusions arrived at on this part of the questions investigated may be summed up as follows:—

1. Acid salts of monobasic acids do not exist in dilute aqueous solutions.

2. Acid salts of polybasic acids, on the contrary, can exist in solution, but generally in a state of partial decomposition.

3. The quantity of the acid salts decomposed on solution increases slowly but continuously with dilution.

4. The quantity decomposed varies also continuously with the ratio between the quantities of neutral salt and free acid present, and in such a way that the stability of the salt is increased by the presence of an excess, either of neutral salt or of free acid.

Division of the same Base between Two Acids.—The experiments in this part of the subject were carried on in a manner precisely similar to those described above. A series of experiments were made on solution of sodium acetate with dilute solutions of hydrochloric, sulphuric, oxalic, and tartaric acids. It was found that each of these acids was able completely to displace the anhydride of the acetate from its metal. Reciprocal experiments, in which acetic acid was added to the solutions of sodium chloride, sulphate, oxalate, and tartrate, confirmed this result.

It was proved also that ammonia has no power to displace the alkali metals from their acetates and oxalates.

The action of oxalic acid on chloride of sodium was next tried. Oxalic acid solution was added to a sufficiently dilute solution of common salt. It was found that about one-tenth of the oxalic acid was converted into sodium bioxalate, about 5 p. c. of the sodium being removed from its combination with the chlorine.

The authors suggest the method here indicated as one likely to have considerable application. J. T. B.

An Improved Gasholder. By F. Mohr (Zeitschr. Anal. Chem., xi, 169—172).

The gasholder is placed in an oval basin of somewhat larger capacity than that of the drum. A zinc tube 70 mm. wide, and 1·3 m. high, provided with a piston holding ½ litre, passes from the upper trough to the bottom of the drum, where it is closed by a caoutchouc valve, through which water enters on raising the piston, the bottom of which is perforated and provided with a caoutchouc valve. By means of this pump arrangement a gasholder of 25 litres capacity can be filled with water in ten minutes. While it is being filled with gas, the displaced water runs into the basin, and remains there ready for use for the next filling with water. This apparatus will be found especially useful as an aspirator, for instance, when it is required to expel a volatile substance from a liquid by continued boiling; this operation, generally very slow, will be accomplished in a very short time by performing it in a current of air, obtained from the gasholder. For this purpose the water is allowed to run out through a long tube, inserted in the side hole at the bottom of the drum, whilst the delivery tube at

the top is connected with the inside of the vessel in which the liquid is boiled.

R. S.

Inorganic Chemistry.

Decolorising Power of Concentrated Ozone. By A. Houzeau (Compt. rend., lxxv, 349—351).

It is well known that ozone is capable of decolorising a large quantity of sulphate of indigo solution; from the author's experiments, indeed, it appears to be about forty times as powerful in this respect as chlorine. The question of oxidation by ozone is, in the author's opinion, rather more complicated than is generally supposed, and, in fact, he has found that in the destruction of the indigo-sulphate colour, there is a production of hydrogen peroxide. This effect can be easily shown in the following manner:—If a few grams of a tolerably concentrated solution of indigo sulphate are decolorised by a flask full of concentrated ozone, the yellow solution will contain peroxide of hydrogen, as may be found by taking a few drops and mixing with ether and chromic acid, when the blue coloration due to perchromic acid, and characteristic of the presence of hydrogen peroxide, is immediately obtained. This will explain the continuous oxidising action which is found to take place in working with ozone. This peroxide of hydrogen may of course be looked at, either as a result of the dehydrogenation of water: $2H_2O - H_2 = H_2O_2$, or simply as the result of the fixation of an extra atom of oxygen.

A. P.

Preparation of Nitrous Acid. By H. Streiff (Deut. Chem. Ges. Ber., v, 285).

The method consists in decomposing the so-called lead-chamber crystals with water. To prepare a concentrated solution of these crystals, dry sulphurous anhydride is passed into well cooled fuming nitric acid until the liquid becomes oily and evolves much nitrous acid (?) on the addition of water. This solution is placed in a flask provided with a doubly bored cork, dropping funnel, &c., and the current of gas regulated at will by the amount of water added.

H. E. A.

Action of Carbon and Iron upon Carbonic Anhydride at a Red Heat. By J. Dumas (Compt. rend., lxxv, 511—519).

The following investigation was undertaken by the author in order to verify or disprove the statement of Dubrunfaut, namely, that "carbonic anhydride cannot be converted into carbonic oxide by ignited charcoal, except through the intervention of hydrogen or water-vapour."

The experiments were conducted with great care.

405 c.c. of liquid hydrochloric acid were submitted to prolonged ebullition, in order to estimate the volume of dissolved air, and 4·6 c.c. were obtained. 100 c.c. of acid would therefore contain 1·15 c.c. of air: but since this quantity of acid would generate 10,000 c.c. of carbonic anhydride, corresponding to 20,000 c.c. of carbonic oxide, the volume of gas incapable of absorption by potash and cuprous chloride should be inappreciable.

In the first experiments, the charcoal employed was not deprived of hydrogen by ignition in a stream of chlorine, but it was recently ignited and perfectly dry. The carbonic anhydride was also dry, and free from any traces of hydrochloric acid vapour.

The following results were obtained:—

	I.	II.	III.	IV.
Carbonic anhydride	0	2	3	12
Carbonic oxide	119	68·5	116	105·8
Gas, non-absorbable and inflammable	1	0·5	1	0·2
	120	71·0	120	118·0

Since non-absorbable and inflammable gas was found in the issuing carbonic oxide, it is obvious that the question was not resolved. Another series of experiments was therefore instituted, in which the carbon was previously ignited in a current of chlorine, and carbonic anhydride passed over it only when hydrochloric acid vapour ceased to be evolved. The results were as follows:—

	I.	II.	III.	IV.
Carbonic anhydride	0·0	0·0	4·6	9·9
„ oxide	99·9	188·0	95·4	90·1
Gas, non-absorbable	0·1	Inappreciable traces.		Inappreciable traces.
	100·0	188·0	100·0	100·0

These results show that at the commencement of the operation, a trace of gas is disengaged which is not absorbed by potash or cuprous chloride, and that this gas finally disappears. Also that towards the termination of the experiment, carbonic anhydride makes its appearance in increasing quantity, having escaped decomposition, because of the deficiency of carbon. The author considers that these two points are definitely settled: first, that charcoal absolutely deprived of hydrogen and water by the action of chlorine, will transform carbonic anhydride into carbonic oxide; secondly, that the conversion is total when the conditions are favourable, that is to say, when there is an excess of carbon, and when the current is slow.

In order to ascertain whether metallic iron exerted a similar decomposing action upon carbonic anhydride, the foregoing experiments were repeated, the tube being filled with clean iron turnings instead of charcoal. It was found that a very slow current of carbonic anhydride passing over iron at a temperature approaching nearly to whiteness,

was not entirely converted into carbonic oxide. For every 100 vols. of carbonic anhydride employed, 30 vols. at least, and sometimes 50 vols., escaped decomposition.

The difference between the action of iron and carbon is explained by the fact that the iron oxide formed tends to reproduce carbonic anhydride by acting upon a portion of the carbonic oxide, and thus gives rise to variable mixtures of the two gases.

J. W.

New Method of Preparing Chromic Acid. By E. Duvillier (Compt. rend., lxxv. 711).

By the following method the whole of the chromic acid contained in barium chromate may be obtained with great ease and despatch.

With 100 parts of water, 100 parts of barium chromate are mixed, and to this 140 parts of nitric acid of 40° strength of Baumé's hydrometer are added. The order of making the mixture is important. The liquid being heated till it becomes red, 200 parts of water are added, and the mixture is boiled for ten minutes. After that the liquid is allowed to cool, when barium nitrate is rapidly thrown down. The liquor, being decanted, is concentrated till its volume becomes about equal to that of the acid used. During this operation nearly all that remains of the barium nitrate is deposited, not more than 0·5 parts of the salt per 100 parts of chromic acid being left. Finally, the excess of the nitric acid used is driven off by evaporating nearly to dryness, adding a little water, evaporating again, and so on several times, till no fumes are observable on testing with a rod wetted with ammonia. The chromic acid may then be easily crystallised out.

It is very nearly pure, and may easily be obtained perfectly pure by precipitating the small trace of barium present with sulphuric acid, evaporating, and crystallising out the chromic acid.

The process here described might be carried out on a large scale. In that case the excess of nitric acid might be condensed, and the barium nitrate formed in the process might be employed for the making of barium chromate.

J. T. B.

Potassium Borofluoride. (Chem. Centr., 1872, 395—398.)

The author gives as the best method of preparing this body, to heat in a flask with upright tube as condenser, the following materials: 156 grams of pure fluor spar, 62 grams of crystallised boric acid, and 327 grams of crude hydrochloric acid, which is then diluted with one half its volume of water. The materials are heated for two or three hours, and the liquid filtered is mixed with potassium chloride, which throws down potassium borofluoride. The salt is washed with water and crystallised from a boiling ammoniacal potash-solution to get rid of some silicofluoride. From these quantities 35 grams of the potassium salt were obtained.

The borofluoride usually forms a crystalline powder, the crystals

belonging to the orthorhombic system, has a density of 2·5, dissolves in 223 parts of water at 20°, and in 15·94 parts at 100°. It is decomposed by standing in aqueous solution, the liquid becoming acid, probably from formation of potassium fluoride and hydrofluoroboric acid; but on evaporation of the solution, the original salt is again formed. When strongly heated, this salt evolves gaseous boron fluoride, as may be seen by heating a little on a platinum wire in a Bunsen burner, when it gives a beautiful green flame. It is decomposed by hydrofluosilicic acid, forming hydrofluoboric acid. A solution of the borofluoride mixed with a solution of silicic hydrate in hydrochloric acid, deposits potassium silicofluoride.

A. P.

Mineralogical Chemistry.

Artificial Formation of Pyroxene and Peridote. By E. Lechartier (Compt. rend., lxxv, 487).

These crystals are formed by heating a mixture of their constituents with calcium chloride. It is not necessary that the constituents be present in the same proportion in which they are united in the crystals, as all those substances which do not enter into their formation, sink as an amorphous and vitrified mass, to the bottom of the crucible. This physical separation was made use of by the author in order to determine the natural groups of definite composition, which are formed on fusing mixtures of calcium chloride with silicic acid, chalk, magnesia, and the oxides of iron and aluminium.

On heating	calcium chloride......	100	grams.
,,	silicic acid	6	,,
,,	chalk	2	,,
,,	magnesia............	2	,,
,,	ferric oxide..........	2	,,
,,	alumina	1	,,

Crystals of pyroxene were thereby obtained, containing only traces of alumina. Pyroxene continued to be formed even when the whole of the silicic acid was added as aluminium silicate in the form of kaolin.

A mixture of	15	grams	kaolin,
,,	6	,,	magnesia,
,,	100	,,	calcium chloride,

yielded crystals of peridote, the surface of which when examined with the microscope, was found to be studded with minute crystals of pyroxene. The presence of a little lime in the peridote thus obtained, is due to this formation of pyroxene.

When the mixture added to the calcium chloride does not contain lime, the formation of pyroxene does not cease altogether, as a certain quantity of lime is furnished by the decomposition of some calcium chloride.

A mixture of calcium chloride with magnesia and silicic acid in the proportion in which they form enstatite:

6	grams	silicic acid,
4	„	magnesia,
100	„	calcium chloride,

yields only a mixture of pyroxene and peridote; if 10 grams of silicic acid be taken, a greater proportion of pyroxene is produced; but when

4	grams of	silicic acid,
6	„	magnesia,
6	„	ferric oxide,

are fused together with calcium chloride, the chief product is peridote with a small quantity only of pyroxene.

Fusion of calcium chloride with chalk, alumina, and silicic acid, or with chalk and kaolin, yields neither wollastonite, nor any other crystalline compound; but the addition of a small quantity of magnesia, causes the formation of pyroxene and peridote crystals.

R. S.

Chemical Composition of Maxite. By H. Laspeyres (J. pr. Chem. [2], v, 470—476).

Maxite is a hydrosulphocarbonate of lead recently found in the Mala-Calzetta mine, near Iglesias, in Sardinia, where it occurs in small quantities in galena, together with anglesite ($PbSO_4$) and cerussite ($PbCO_3$). It occurs in curvilaminar and crystalline masses, with one distinct cleavage-plane, to which the acute bisectrix is perpendicular. The cleavage and the optical properties show that the mineral belongs to the rhombic or trimetric system. Besides the principal cleavage, which yields lamellæ with adamantine lustre and Newtonian colour rings, there appear to be also indistinct directions of cleavage. The mineral is negatively uniaxial, with very small axial angle, and strong refractive power, like all native lead-salts. Dispersion $\rho < v$. Fracture conchoïdal or splintery. Hardness 2·5 to 3, that is, between potash-mica and calcspar: sp. gr. 6·874. Somewhat brittle; colourless; transparent to translucent. Lustre on the fractured surface, fatty-adamantine like that of cerussite. In physical properties, therefore, maxite closely resembles leadhillite ($3PbCO_3.PbSO_4$).

The qualitative analysis of maxite shows the presence of lead oxide, carbonic acid, sulphuric acid, and water, and the complete absence of chlorine, silver, arsenic, antimony, and copper. Like leadhillite and lanarkite, it dissolves but partially in water, but easily and with strong effervescence in nitric acid, either strong or weak, leaving a residue of lead sulphate in the form of fine bluish-white scales; in somewhat stronger nitric acid it dissolves completely with the aid of heat. Heated in a tube it decrepitates strongly, exfoliates, becomes white and opaque like gypsum, and gives off water, whereby it is at once distinguished from lanarkite ($PbCO_3.PbSO_4$) and leadhillite ($3PbCO_3.PbSO_4$). At 100° only traces of hygroscopic water (0·099 p.c.) are given off, the constitutional water requiring a heat of 250°—300° to expel it. The

carbonic acid requires a still higher temperature, and is not completely expelled below a bright red heat. At the outer edge of an ordinary spirit-flame, the mineral fuses quickly and quietly, almost as easily as native sulphide of antimony (which, as v. Kobell has shown, is the most easily fusible of all minerals) to a bead of lead sulphate and oxide, which is red while hot, then becomes yellow, and, on cooling, crystalline and nearly white. Before the blowpipe it gives the ordinary reactions of lead, and when fused with sodium carbonate on charcoal, a strong hepatic reaction.

Quantitative analysis gave results agreeing with the empirical formula, $5H_2O$, $18PbO$, $9CO_2$, $5SO_3$.

	Calculation.		Analysis.
$5H_2O$	90	1·838	1·866
$9CO_2$	386	8·081	8·082
$5SO_3$	400	8·163	8·140
$18PbO$	4014	81.918	81·912
	4890	100·000	100·000

From this may be deduced the rational formula, $5PbSO_4.9PbCO_3.(4PbO·5H_2O)$, which is that of a molecular compound of 31 p.c. lead sulphate, 49 lead carbonate, and 20 p.c. of a lead hydrate or hydroxide, not known in the separate state.

H. W.

Guadalcazarite, a New Mineral. By THEODOR PETERSEN (J. pr. Chem. [2], v, 80).

THIS mineral is a sulphate of mercury and zinc, containing a little selenium, occurring with quartz and baryta, at Guadalcazar in Mexico, where also cinnabar is found in abundance.

The new mineral is massive, crypto-crystalline, iron-black with a slight bluish tinge, opaque even in thin laminæ; of fatty metallic lustre, uneven conchoidal fracture and black streak; rather brittle, and so soft that it may easily be rubbed to a greyish-black powder. Hardness = 2. Sp. gr. = 7·15 at 15°. The lumps exhibit here and there a thin coating of cinnabar.

On charcoal before the blowpipe it decrepitates strongly, then gives off fumes of mercury, and an odour of selenium; and after prolonged blowing leaves yellowish-white zinc oxide, which, if it has not been too strongly heated, exhibits an iridescent tarnish here and there, and a distinct reaction of cadmium. Heated in an open glass tube, it yields a grey to black sublimate containing mercury, mercuric sulphide, and mercuric selenide, sulphurous acid being also perceptible, and finally leaves yellowish oxide of zinc. Aqua regia dissolves it easily, with separation of a small quantity of sulphur.

Quantitative analysis gave the following numbers:—

S.	Se.	Hg.	Zn.	Cd.	Fe.
14·58	1·08	79·73	4·23	distinct trace.	trace = 99·62.

agreeing nearly with the formula, 6HgS.ZnS, which requires 15·05 p.c. S., 80·58 Hg., and 4·37 Zn.

Though the composition of guadalcazarite does not differ greatly from that of cinnabar, the properties of the two minerals are quite distinct. An ore from Culebras, in Mexico, examined some time ago by Del Rio (*Pogg. Ann.*, xxxix, 526), and containing selenium, sulphur, and mercury, was a mixture of several minerals. The highly seleniferous, nearly lead-grey onofrite of San Onofre, in Mexico, is also quite distinct from guadalcazarite.

H. W.

On the Gases Enclosed in certain Lignites (Preliminary Notice). By Kolbe and Zitowitsch (J. pr. Chem. [2], v, 79).

The gas which accumulates in lignite mines has long been recognised as consisting mainly of carbon dioxide, whereas marsh-gas has never been detected in it. The great oxidability of lignite has been demonstrated by the experiments of Varrentrapp (*Chem. Centr.*, 1865, p. 953).

The gases enclosed in Bohemian patent lignite, and in an earthy lignite of inferior quality, have been examined by Zitowitsch. The mode of collection was the same as that adopted by v. Meyer with pit coal (p. 798 of last volume). The quantity obtained from both varieties was small, and was not determined. The gases were found to consist of carbon dioxide, carbon monoxide, nitrogen and oxygen, in the following proportions:—

Gas from	CO_2.	CO.	N.	O.
I. } Bohemian lignite	89·66	1.80	8·03	0·51
II. } Bohemian lignite	82·40	3·00	14·15	0·45
III. Earthy lignite	83·99	1·04	14·91	0·65

H. W.

Organic Chemistry.

Trimethyl-ethyl-formene. By Gabainow (Deut. Chem. Ges. Ber., v, 479).

Trimethyl-ethyl-formene $C\left\{\begin{matrix}(CH_3)_3\\ C_2H_5\end{matrix}\right.$ is produced by the action of zinc-ethyl on tertiary butyl iodide; it is a liquid boiling at 43°—48°.

C. S.

Action of Hydrochloric Acid on Isobutylene. By Zalessky (Deut. Chem. Ges. Ber., v, 480).

On heating this hydrocarbon with concentrated hydrochloric acid to 100°, it is converted into tertiary butyl chloride, the action of hydrochloric acid being therefore analogous to that of hydriodic acid.

C. S.

The Constitution of Sodium Ethylate. By A. LAUBENHEIMER (Ann. Chem. Pharm., clxiv, 280—283).

THERE are three possible ways of expressing the constitution of sodium ethylate, namely—

I.	II.	III.
CH_3	CH_2Na	CH_3
CH_2	CH_2	$CH.Na$
ONa	OH	OH.

If the first formula is the true one, the action of ethyl iodide on sodium ethylate ought to yield ethylic ether; if the second is correct, normal butylic alcohol should be obtained; and finally, if the third formula correctly expresses the constitution of sodium ethylate, the action of ethyl iodide on it should give secondary butylic alcohol.

The action of ethylic iodide on sodium ethylate carefully freed from alcohol was tried, and the product was found to be ethylic ether, accompanied by a small quantity of ethylene. The author considers that this latter arises from a secondary reaction, according to the subjoined equation—

$$C_2H_5ONa + C_2H_5I = NaI + C_2H_4 + C_2H_5OH.$$

This action is analogous to the decomposition of ethyl iodide by sodium hydrate, and to the formation of butylene by the action of alcoholic potash on butyl iodide.

These results have satisfied the author that the true formula of sodium ethylate is C_2H_5ONa, and not that proposed by Wanklyn, $C_2H_4Na.OH$.

T. B.

Investigation of Propyl Compounds. By I. PIERRE and E. PUCHOT (Compt. rend., lxxv, 520).

THE authors have already shown that propylic alcohol is a constant product of alcoholic fermentation. They have separated and purified large quantities of this alcohol, and in a previous memoir have described the principal ethers of the series. They now offer some new facts relating to propionic acid.

Propionic acid brought to its maximum degree of concentration contains the elements of one molecule of water, which cannot be removed by fractional distillation. It may therefore be represented by the formula $C_3H_6O_2$ or $C_6H_{10}O_3.H_2O$. Its sp. gr. is 1·0143 at 0°, 0·9607, at 49·6°, 0·9062, at 99·8°. It boils regularly at 146·6° under a pressure of 760 mm.

Barium propionate contains one molecule of water of crystallisation, and is represented by the formula—

$$Ba(C_3H_5O_2)_2 + H_2O, \text{ or } C_6H_{10}O_3.H_2O.BaO.$$

Silver propionate is anhydrous and represented by the formula—

$$AgC_3H_5O_2, \text{ or } C_6H_{10}O_3.Ag_2O.$$

J. W.

Secondary Amyl Alcohol. By Flawitzky (Deut. Chem. Ges. Ber., v, 479).

This alcohol is formed, according to Berthelot, by the action of sulphuric acid on amylene; but Erlenmeyer contradicts this statement. By using Butlerow's apparatus (*Ber.*, iii, 422), and passing a mixture of carbon dioxide and amylene-vapour into dilute sulphuric acid, more than half of the amylene is absorbed, whilst the remainder is condensed to diamylene. On distilling the acid solution with water, it yields secondary amyl alcohol boiling at 102°—104°.

C. S.

Vinyl Bromide. By E. Fuchs (Deut. Chem. Ges. Ber., v, 765).

In order to obtain experimental evidence of the correctness of Kolbe's formula for styrolene, $\left.\begin{array}{l} CH \\ CH \\ CH \\ C_2H_3 \\ H_2 \end{array}\right\} C_3$ (*i.e.*, to show that styrolene is vinylated benzene), the author treated vinyl bromide and phenyl bromide with sodium: no action ensued in a bath of snow and salt; at 10°—12° a vigorous action set in, and some diphenyl was formed; when the mixture was heated to 60°, 100°, or 110° in sealed tubes, acetylene was also produced; but no styrolene was formed in any case.

Vinyl bromide is decomposed by sodium at 110° in accordance with the equation:—

$$2C_2H_3Br + Na_2 = C_2H_2 + C_2H_4 + 2NaBr.$$

The author hence concludes that the idea that styrolene contains in its formula a benzene radical, is destitute of experimental proof.

C. R. A. W.

Note by Abstractor.—Much the same results were obtained some time ago by the abstractor on attempting to synthesize styrolene from nascent vinyl chloride and phenyl bromide by the action of sodium: acetylene and benzene were formed instead of styrolene: a little diphenyl also was produced. Attempts to prepare styrolene from ethylene dichloride and ordinary solid dibromobenzene by this reaction:—

$$C_2H_4Cl_2 + C_6H_4Br_2 + 4Na = 2NaCl + 2NaBr + C_6H_4{=}C_2H_4,$$

were equally unsuccessful: so that it would appear doubtful whether styrolene is really either vinylated benzene, or the ethylenated benzene corresponding to ordinary dibromobenzene.

C. R. A. W.

Action of Silver Nitrate on Cane Sugar. By BORODULIN (Deut. Chem. Ges. Ber., v, 477).

MAUMENÉ states that by this reaction an inactive sugar is produced, but the author obtained only some inverted sugar, together with silver cyanide and oxalate.

C. S.

Action of Potassium Permanganate on Milk-sugar. By A. LAUBENHEIMER (Ann. Chem. Pharm., clxiv, 283—288).

THE complete oxidation of milk-sugar may be effected by a warm alkaline solution of potassium permanganate:

$$C_{12}H_{22}O_{11}.H_2O + 24O = 12CO_2 + 12H_2O.$$

This equation was proved by an estimation of the quantity of manganese peroxide set free.

An attempt to form isomalic acid or malic acid by heating milk-sugar with the quantity of potassium permanganate indicated by the subjoined equation, led only to the formation of oxalic acid, and one or two uncrystallisable acids, perhaps identical with the gallactic acid and pectolactic acid of Boedeker and Struckmann.

$$C_{12}H_{22}O_{11}.H_2O + 4MnKO_4 = 3C_4H_6O_5 + 4MnO_2 + 4KHO + H_2O.$$

T. B.

Action of Iodide of Nitrogen upon Starch, &c. By M. HUSSON, jun. (Compt. rend., lxxv, 549).

THE author has endeavoured to prepare albumin artificially by the action of iodide of nitrogen upon starch, gum-senegal, &c., aided by atmospheric oxygen and solar light. The experiments were, however, invariably unsuccessful, the decomposition of the iodide being generally attended with evolution of nitrogen. At all events, no organic compound containing nitrogen was formed. The action of iodide of nitrogen upon albumin was then studied; but in this instance also, no very decided result was obtained. The albumin subsequently precipitated, appeared to contain iodine, but the iodised compound readily decomposed when exposed to light: indeed the caustic ammonia employed in the preparation of the iodide appeared to have more action upon the albumin than the iodide of nitrogen itself. The author is of opinion that the iodine replaces sulphur, and not hydrogen in the albumin, but offers no evidence in support of this conclusion.

J. W.

Action of Yeast on Sugar-solutions. By J. W. GUNNING (Deut. Chem. Ges. Ber., v, 821).

FRESH yeast was well washed with water on a sieve and poured on a cloth; the residue diffused through glycerin and kept in a warm place for some days, gave rise to a slight fermentation; after filtration by

means of a Bunsen pump, a solution was obtained which readily converted cane-sugar into glucose and had an acid reaction; alcohol threw down an inactive precipitate, and heat coagulated the liquid, indicating the presence of an albuminoïd. Much nitrogen was obtained, also phosphoric acid and sulphur. After repeated washing with glycerin, the cellular substance left on the filter had entirely lost the property of causing fermentation, but exhibited no change of structure under the microcope. On addition of some of the ferment-solution, the power of causing fermentation in glucose and of changing cane-sugar into glucose was regained.

Fresh yeast, well washed and dried at 110°, contained N = 9·57 to 10·13; acids 10·33, containing of phosphoric acid 5·42; whilst the yeast exhausted with glycerin as above, contained N = 8·34 to 8·82; acids 7·72, containing of phosphoric acid 4·0.

This exhausted yeast did not act on Pasteur's solution; but the filtrate readily set up fermentation, showing that the action is accelerated by the presence of ammoniacal salts: sodium chloride, magnesium chloride, and the other salts of sea-water gave analogous results.

C. R. A. W.

Glycerin as a Solvent. By KLEVER (Chem. Centr., 1872, 434).

ONE hundred parts by weight of glycerin dissolve at ordinary temperatures:—

Parts by weight.		Parts by weight.	
20	.. Arsenious oxide.	20	.. Morphine hydrochloride.
20	.. Arsenic oxide.	0·20	.. Phosphorus.
10	.. Benzoic acid.	20	.. Lead acetate.
10	.. Boric acid.	50	.. Potassium arsenate,
15	.. Oxalic acid.	3·50	.. Potassium chlorate.
50	.. Tannic acid.	25	.. Potassium bromide.
40	.. Alums.	32	.. Potassium cyanide.
20	.. Ammonium carbonate.	40	.. Potassium iodide.
20	.. Ammonium chloride.	0·50	.. Quinine.
5·50	.. Tartar-emetic.	0·25	.. Quinine tartrate.
3	.. Atropine.	50	.. Sodium arsenate.
33	.. Atropine sulphate.	8	.. Acid sodium carbonate.
10	.. Barium chloride.	60	.. Borax.
2·20	.. Brucine.	98	.. Sodium carbonate.
5	.. Calcium sulphide.	20	.. Sodium chlorate.
0·50	.. Cinchonine.	0·10	.. Sulphur.
6·70	.. Cinchonine sulphate.	0·25	.. Strychnine.
10	.. Cupric acetate.	4	.. Strychnine nitrate.
30	.. Cupric sulphate.	22·50	.. Strychnine sulphate.
7·50	.. Mercuric chloride.	50	.. Urea.
27	.. Mercuric cyanide.	1	.. Veratrine.
1·9	.. Iodine.	50	.. Zinc chloride.
0·45	.. Morphine.	40	.. Zinc iodide.
20	.. Morphine acetate.	35	.. Zinc sulphate.

H. W.

Trimethylacetic Acid. By BUTLEROW (Deut. Chem. Ges. Ber., v, 478).

THE nitrile of this acid could not be obtained by the action of silver cyanide on tertiary butyl iodide, and by using potassium cyanide only traces are produced. But by acting with the iodide upon dry mercuric cyanide, the following reaction is produced:—

$$C_4H_9I + Hg(CN)_2 = C_4H_9CN + HgICN.$$

The reaction is very violent; some isobutene is evolved, and polymeric isobutenes are formed, besides the nitrile. The latter compound boils at about 103°, and yields by heating with alcoholic potash, the potassium salt of trimethyl-acetic acid The pure acid dried over phosphoric pentoxide, boils at 161°, and solidifies on cooling to a glassy mass mixed with crystals. It melts at 34°—35°, and is but sparingly soluble in water, and not deliquescent The barium salt $(C_5H_9O_2)_2Ba + 5H_2O$, crystallises in needles grouped in stars, and is readily soluble in water. The silver salt, $C_5H_9O_2Ag$, is a white precipitate, consisting of small plates, crystallising from a hot neutral solution in long plates, and from an acid solution in small needles.

C. S.

Action of Monobromacetyl Bromide on Zinc Methide. By SHDANOW (Deut. Chem. Ges. Ber., v, 479)

BY this reaction the author obtained an alcohol boiling at 110°—112°, which is probably a hexyl alcohol, $C_6H_{14}O$. On oxidizing it with chromic acid solution, it yielded acetic acid, and a small quantity of acetone.

C. S.

Action of Monobromacetyl Bromide on Zinc Ethide. By ANITOW (Deut. Chem. Ges. Ber., v, 479).

THIS reaction yields a decyl alcohol, $C_{10}H_{22}O$, boiling at 155°—157°.

C. S.

Reduction of Ethyl Orthoformate. By A. LADENBURG (Deut. Chem. Ges. Ber., v, 752).

ETHYL orthoformate was repeatedly treated with zinc-ethyl and sodium, in a manner similar to that adopted by the author in the case of orthosilicic ether. The product was separated into two portions, one of which boiled at 142°—144°, while the other passed over at about 100°. The higher portion, which appeared to consist principally of unaltered ethyl orthoformate, gave indications of the presence of propionic aldehyde, but this body was not distinctly recognised. By treating the lower portion with sulphuric acid, and washing the residue, a hydrocarbon was obtained, having the formula, C_7H_{16}. This heptane, which the author regards as a new variety (triethyl methane) is a colourless liquid, with a faint petroleum-like odour. It boils at 96°, and has a

specific gravity of 0·689 at 27°. A determination of its vapour-density led to the number 101·5; the formula C_7H_{16} indicates 100.

T. B.

Reduction-products of Silicic Ether and its Derivatives. By A. LADENBURG (*Ann. Chem. Pharm.*, clxiv, 300—331).

WHEN silicic ether is acted on by zinc-ethyl and sodium jointly, an action ensues, which is tantamount to an abstraction of oxygen from the ether, producing successively, $Si(C_2H_5)(OC_2H_5)_3$, $Si(C_2H_5)_2(OC_2H_5)_2$, and $Si(C_2H_5)_3(OC_2H_5)$, boiling at 159°, 155·5°, and 153° respectively; probably the action consists in a replacement of the (OC_2H_5) group by (C_2H_5) from the zinc-ethyl, zinc ethylate being thus produced. The author's experiments on this point are not yet concluded.

1. *Orthosilicopropionic ether*, $Si(C_2H_5)(OC_2H_5)_3$, is thus produced much more readily than by the process originally described, viz., treatment of the chloride $SiCl(OC_2H_5)_3$ with zinc-ethyl and sodium. When warmed with hydriodic acid of boiling point 127°, it decomposes, in accordance with the equation:

$$SiC_2H_5(OC_2H_5)_3 + 3HI = Si(C_2H_5)O_2H + 3C_2H_5I + H_2O,$$

silicopropionic acid being thus formed; this is, in fact, the most convenient way of preparing the body.

When heated with benzoyl chloride, orthosilicopropionic ether undergoes the reaction:

$$SiC_2H_5(OC_2H_5)_3 + 3C_7H_5OCl = SiC_2H_5Cl_3 + 3C_7H_5O_2(C_2H_5),$$

ethyl benzoate and *silicopropionic trichloride* (*silicon-ethyl trichloride*) being produced. This latter has not been obtained perfectly pure; it boils at about 100°, and is decomposed by moist air; water or aqueous ammonia produces hydrogen chloride and silicopropionic acid.

Phosphorus pentachloride appears to act on orthosilicopropionic ether, in accordance with the reaction:

$$SiC_2H_5(OC_2H_5)_3 + PCl_5 = SiC_2H_5(OC_2H_5)_2Cl + POCl_3 + C_2H_5Cl;$$

a remarkable action, as the rule is that bodies containing (OC_2H_5) associated with carbon, are *not* attacked by phosphorus pentachloride (Henry, *Deut. Chem. Ges. Ber.*, 1869, 664).

2. *Silicondiethyl ether*, $Si(C_2H_5)_2(OC_2H_5)_2$, boils at 155·8°, has the specific gravity 0·8752 at 0°, and the vapour-density 173·9 (calculated 176); it is stable in the air, insoluble in water, soluble in alcohol and in ether; unlike orthosilicopropionic ether, it does not yield silicopropionic acid by the action of concentrated sulphuric acid, and is not attacked by alcoholic ammonia; it is acted on by concentrated potash-ley only after several hours' heating, the reaction being probably

$$Si(C_2H_5)_2(OC_2H_5)_2 + 4KHO + 2H_2O = SiC_2H_5O_2K + 3C_2H_3O_2K + 7H_2.$$

When silicondiethyl ether and acetyl chloride are heated together to 200°

in a sealed tube in the proportions denoted by the following formulæ (the former slightly preponderating) a reaction takes place represented by the equation,

$$Si(C_2H_5)_2(OC_2H_5)_2 + C_2H_3OCl = C_2H_3O_2(C_2H_5) + Si(C_2H_5)_2Cl(OC_2H_5),$$

silicondiethyl-chlorethylin being formed, which boils between 146° and 148°, and is changed by contact with water into a viscid oil, free from chlorine. If, however, *two* proportions of benzoyl chloride and one of silicondiethyl ether are heated to 250°, *silicondiethyl chloride*, ($Si(C_2H_5)_2Cl_2$, is produced, boiling between 128° and 130°; the vapour of this body mixed with air is explosive. Water decomposes it, forming hydrogen chloride, and a syrupy substance which contains no chlorine: this is *silicondiethyl oxide*, $Si(C_2H_5)_2O$; it may be more conveniently procured by the action of aqueous hydriodic acid (boiling at 127°) upon silicondiethyl ether, according to the equation,

$$Si(C_2H_5)_2(OC_2H_5)_2 + 2HI = Si(C_2H_5)_2O + H_2O + 2C_2H_5I.$$

It is a thick syrup, distilling unhanged above the boiling point of mercury, not solidifying at −15°; it is insoluble in water, difficultly soluble in alcohol, and readily soluble in ether.

From its formula and origin this body appears to be diethyl ketone in which Si replaces C; unlike carbon ketones, however, it does no combine with nascent hydrogen to form a sort of carbinol; moreover it yields silicopropionic acid on boiling for a day, with concentrated soda-ley, whereas diethyl ketone yields only acetic acid by oxidation (Chapman and Smith). It forms a notable exception to Mendelejeff's rule that silicon compounds boil at a lower temperature than the corresponding carbon compounds, as do also the following bodies:—

	Boiling-point.		Boiling-point.
$Si(OC_2H_5)_4$	166·5°	$C(OC_2H_5)_4$	128°
$Si(C_2H_5)_3OH$	154·0°	$C(C_2H_5)_3OH$	141°
$Si(C_2H_5)_3H$	107°	$C(C_2H_5)_3H$	96°
$Si(CH_3)_4$	30°	$C(CH_3)_4$	9°

3. *Silicontriethyl ether* or *silicoheptyl ether*, $Si(C_2H_5)_3(OC_2H_5)$, boils at 153°, and has the specific gravity 0·8393 to 0·8414 at 0°, and the vapour-density 161·6° (calculated 160°); it is stable in the air, soluble in ether and alcohol, and insoluble in water. It is not attacked by alcoholic ammonia, or by aniline at 250°, but is decomposed by water at that temperature; it is soluble in concentrated sulphuric acid, wherein it differs from silicon-ethyl.

Acetyl chloride acts on silicon-triethyl ether at 180°, thus—

$$Si(C_2H_5)_3(OC_2H_5) + C_2H_3OCl = Si(C_2H_5)_3Cl_3 + C_2H_3O_2(C_2H_5)$$

producing *silicoheptyl chloride*, boiling at 143·5°; ammonia and aniline decompose, thus giving liquids containing silicon; mercury cyanide has no action on it, nor can the chlorine be replaced by hydrogen by means of nascent hydrogen.

If heating of the solution be avoided, aqueous ammonia acts in accordance with the reactions:

$$Si(C_2H_5)_3Cl + NH_3 + H_2O = NH_4Cl + Si(C_2H_5)_3OH$$
$$2Si(C_2H_5)_3Cl + H_2O = Si_2(C_2H_5)_6O + 2HCl,$$

triethylsilicol and *silicoheptyl oxide* being produced. The former of these is more easily produced by heating acetic anhydride and silicoheptyl-ethyl ether to 250°, whereby the following reaction takes place :—

$$Si(C_2H_5)_3(OC_2H_5) + (C_2H_3O)_2O = C_2H_3O(OC_2H_5) + Si(C_2H_5)_3(OC_2H_3O).$$

triethysilicoheptyl acetic ether being formed; this boils at 168°, and yields triethylsilicol on long-continued boiling with sodium carbonate.

Triethylsilicol, or *Silicoheptyl Hydroxide*, is a thick colourless fluid, of camphor-like odour, insoluble in water, soluble in alcohol and ether; it exhibits alcoholic characters (whence the name), undergoing the following reactions :—

A. $Si(C_2H_5)_3OH + C_2H_3OCl = HCl + Si(C_2H_5)_3(OC_2H_3O)$,

the resulting product being, however, decomposed by the hydrochloric acid as fast as it is formed, thus :—

$$Si(C_2H_5)_3(OC_2H_3O) + HCl = C_2H_4O_2 + Si(C_2H_5)_3Cl.$$

B. Sodium evolves hydrogen, giving *sodium silicolate* $Si(C_2H_5)_3ONa$.

C. An ethereal solution of this latter yields, on passing carbon dioxide into it, an amorphous body, which is *silicoheptyl-sodium carbonate*,

$$Si(C_2H_5)_3O.CO.ONa.$$

When heated to redness, this body decomposes, thus :—

$$2Si(C_2H_5)_3CO_3Na = CO_2 + Na_2CO_3 + \{Si(C_2H_5)_3\}_2O$$

being the first silicon-containing body that leaves carbonate instead of silicate when heated.

D. Hydriodic acid of boiling point 127°, causes the following reaction to take place at 200°.—

$$Si(C_2H_5)_3OH = C_2H_6 + Si(C_2H_5)_2O.$$

E. Oxidising agents, such as chromic and permanganic acids, have no action; Nordhausen sulphuric acid, however, causes the reaction—

$$Si(C_2H_5)_3OH + SO_3 = Si(C_2H_5)O_2H + 2C_2H_4 + H_2 + SO_2.$$

silicopropionic acid being thus produced, by a reaction analogous to that which tertiary alcohols undergo by oxidation (Butlerow, *Deut. Chem. Ges. Ber.*, 1871, 931).

F. Dehydrating agents, such as phosphoric anhydride, convert triethyl-silicol into its corresponding ether, *silicoheptyl oxide*, $\{Si(C_2H_5)_3\}_2O$.

Silicoheptyl oxide may also be obtained by the action of hydriodic or sulphuric acid on silicoheptyl-ethyl ether, or by that of potash-ley on silicontriethyl chloride or bromide. It is a colourless, syrupy liquid,

boiling at 231°, and of specific gravity 0·859 at 0°; it is soluble in sulphuric acid, and separates thence unchanged on dilution, if heating be avoided; otherwise some triethylsilicol is formed.

4. *Silicoheptyl hydride*, $Si(C_2H_5)_3H$, is the last product of the action of sodium and zinc-ethyl on silicic ether; it boils at 107°, and resembles the petroleum hydrocarbons in smell; it is insoluble in water and in concentrated sulphuric acid, soluble in ether and alcohol. It is stable in the air, and burns with a brilliant flame, leaving silica; its specific gravity at 0° is 0·751, and its vapour-density 118·4 (calculated 116). Nitric acid and Nordhausen sulphuric acid attack it readily, the latter producing the reaction—

$$2Si(C_2H_5)_3H + 2SO_3 = H_2O + 2SO_2 + Si_2(C_2H_5)_6O.$$

Bromine added drop by drop to the well cooled liquid, gives hydrogen bromide and *silicoheptyl bromide*, $Si(C_2H_5)_3Br$, boiling at 161°, and forming silicontriethyl oxide by the action of caustic alkalies, also triethylsilicol with ammonia.

Simultaneously with silicoheptyl hydride, *silicon-ethyl*, $Si(C_2H_5)_4$ is formed by the action of zinc-ethyl and sodium on silicic ether; the body obtained boiled at 151°—153°, and had the properties of the siliconethyl of Friedel and Crafts.

A small quantity of high-boiling silico-carbonaceous substances was also formed, probably reduction-products of polysilicic-ethers.

It is noticeable that the specific gravity of the silicon-ethyl-oxethyl series diminishes with the diminution in oxygen, but not regularly—

$Si(C_2H_5)_4O_4$	0·9676
$Si(C_2H_5)_4O_3$	0·9207
$Si(C_2H_5)_4O_2$	0·8752
$Si(C_2H_5)_4O$	0·8403
$Si(C_2H_5)_4$	0·8341

The substitution of C_2H_5 for Cl raises the boiling point—

$SiCl_4$	58°				
$SiCl_3C_2H_5$	100	$SiCl_3C_2H_5O$	104°		
$SiCl_2(C_2H_5)_2$	129°	$SiCl_2(C_2H_5)_2O$	?	$SiCl_2(C_2H_5)_2O_2$	137°
$SiCl(C_2H_5)_3$	143·5°	$SiCl(C_2H_5)_3O$	147°	$SiCl(C_2H_5)_3O_2$	151°
$Si(C_2H_5)_4$	152°	$Si(C_2H_5)_4O$	153°	$Si(C_2H_5)_4O_2$	155·5°

$SiCl(C_2H_5)_3O_3$	156°		
$Si(C_2H_5)_4O_3$	159°	$Si(C_2H_5)_4O_4$	166·5°

C. R. A. W.

Silico-Acetic Anhydride. By FRIEDEL and LADENBURG (Ann. Chim. Phys. [4], xxvii, 428—432).

BY the action of silicic chloride on acetic acid or acetic anhydride, the authors have obtained a mixed anhydride, $Si(C_2H_3O_2)_4$, derived from silicic acid and acetic acid. It is best obtained by digesting silicic chloride with a mixture of acetic acid and acetic anhydride;

on cooling, the silico-acetic anhydride is deposited in beautifully white crystals, apparently belonging to the quadratic system.

Silico-acetic anhydride when dropped into water is decomposed with a hissing noise, gelatinous silica and acetic acid being formed. It cannot be distilled under the ordinary pressure, as it is decomposed at a temperature of 160°—170° into silica and acetic anhydride; but if the pressure be reduced to 5 or 6 millimeters, it passes over unchanged at about 148° and condenses in beautiful white crystalline masses, melting at about 110°. It is decomposed by alcohol, with formation of ethyl acetate and gelatinous silica; cold ether, however, does not change it, although when heated to 200° with that substance it splits up into silica and acetic anhydride. With dry ammonia it yields acetamide and hydrated silica.

This anhydride corresponds with the silicic ether of Ebelmen $Si(C_2H_5O)_4$; and the compound $Si(C_2H_5O)_3(C_2H_3O_2)$, formerly obtained by one of the authors in conjunction with Crafts, may be regarded as an ethylic derivative of silico-acetic anhydride.

When acetic acid not quite free from water is treated with silicic chloride, a gelatinous mass is obtained, which perhaps contains mixed anhydrides corresponding to the polysilicic ethers.

Phosphorus trichloride reacts on acetic anhydride, forming a white powder, which contains the elements of acetic acid and phosphorous acid, together with chlorine. Attempts to remove the latter were unsuccessful. Titanium chloride also gave a solid body with acetic anhydride, but the authors have not yet studied its properties.

Broughton has observed that when lead acetate is heated with carbon disulphide, the products of the reaction are lead sulphide, acetic anhydride, and carbonic anhydride. The authors think it probable that in this case a mixed aceto-carbonic anhydride is first formed, and that this afterwards splits up into carbonic anhydride and acetic anhydride. T. B.

A Silicic Mercaptan and a Silicic Chlorobromide. By FRIEDEL and LADENBURG (Ann. Chim. Phys. [4], xxvii, 416—428).

THE silicic chlorosulphide of Pierre being the only volatile compound of silicon, the composition of which does not appear to agree with the new atomic weight of that element, the authors have undertaken its re-examination. In its preparation they followed the directions of Pierre, and they succeeded in separating from the product a fraction boiling at 95°—97°, which they consider to be Pierre's compound in a state of purity. The authors' analyses indicated the presence of hydrogen, and led them to adopt the formula $SiCl_3SH$ ($Si = 28$) in place of that given by Pierre, $SiCl_2S$, ($Si = 21$). The formula $SiCl_3SH$ was confirmed by a determination of the vapour-density, which was found to be 5·78, the theoretical number being 5·83. This compound is therefore a *silicic chlorsulphydrate*, which may be considered as a trichloride of sulphosilicic acid.

This *silicic chlorsulphydrate* is a colourless liquid, boiling at 96°,

and possessing a mixed odour of hydrochloric acid and hydrosulphuric acid, these two acids being formed, together with silica, when it is exposed to the air. When three molecules of alcohol are made to react on one molecule of silicic chlorosulphydrate, an evolution of hydrochloric acid takes place, and a compound, $SiSH(OC_2H_5)_3$ appears to be produced; but if either this compound or the original silicic chlorosulphydrate be treated with excess of alcohol, a reaction, resulting in the formation of silicic ether, $Si(C_2H_5O)_4$ takes place. Bromine decomposes silicic chlorosulphydrate with formation of *silicic trichlorobromide*, $SiSHCl_3 + Br_3 = SiBrCl_3 + SBr + HBr$.

Silicic trichlorobromide, the probable formation of which has been indicated by the authors in their investigations on the action of bromine on silicochloroform, boils at 80°, and has a vapour-density of 7·25, the theoretical density being 7·42. It is a colourless fuming liquid, decomposed by water, and possessing a great similarity to silicium chloride.

Among the products of the action of bromine on silicochloroform, the authors have found, in the portion boiling at about 100°, a second silicic chlorobromide, $SiBr_2Cl_2$.

The silicic trichlorosulphydrate described in this paper is analogous to the sulphydrates of the hydrocarbon radicals or mercaptans: it ought therefore to be considered as an analogue of methyl-mercaptan, CH_3SH, and according to the nomenclature used by the author for other silicated compounds, it should be called *trichlorsilicomercaptan*. This analogy has been further illustrated by the authors' study on the action of bromine on ethyl-mercaptan, the results being precisely analogous to those obtained by the action of bromine on trichlorsilicomercaptan—

$$C_2H_5SH + Br_3 = C_2H_5Br + SBr + HBr.$$

T. B.

Preparation of Propionic Acid from Lactic Acid. By A. FREUND (J. pr. Chem. [2], v, 446—452).

THE formation of propionic acid by the action of hydriodic acid on lactic acid, originally observed by Lauteman, has been confirmed by the author, who finds, moreover, that this reaction affords a convenient method for the preparation of propionic acid.

60 grams of iodine are suspended in 140 grams of water, converted into hydriodic acid by means of hydrosulphuric acid, and the hydriodic acid thus obtained is placed in a retort with 60 grams of lactic acid, after which the mixture is distilled until about 100 grams of liquid have passed over. A condensing tube being now adapted to the apparatus, the contents of the retort are digested for about four hours, when the iodine, which by this time has crystallised in the condensing tube, is washed back into the retort with the 100 grams of distillate previously drawn off, and hydrosulphuric acid is passed through the mixture in order to rehydrogenise the free iodine. The deposited sulphur being removed, 100 grams are again distilled off, the contents of the retort are digested during another period of four hours, and this series of operations is repeated six or seven times, the

whole of the lactic acid being by this time converted into propionic acid, almost the whole of which is contained in the 100 grams drawn off after the last digestion. This distillate is now mixed with 50 grams of water, and distilled as long as the contents of the receiver contain only traces of hydriodic acid; the distillate is then neutralised with sodium carbonate, and sufficient lead propionate is added to convert the sodium iodide into sodium propionate. The solution is then evaporated, and the dry sodium propionate is decomposed with hydrochloric acid gas, as directed by Linneman (*Ann. Chem. Pharm.*, clx, 197).

Lactic acid, when treated in this way, yielded about 62 per cent. of pure sodium propionate.

The author failed to detect acetic acid among the products of the above reaction, but observed the formation of aldehyde, of a gas burning with a blue flame, and that of a small quantity of a substance crystallising from alcohol in long shining needles.

T. B.

Isobutyric Acid. By I. PIERRE and E. PUCHOT (Compt. rend., lxxv, 1006—1007).

THE butyric acid, obtained by the oxidation of fermentation butylic alcohol, boils at 155·5° under the normal pressure of 760 mm., and has a density of ·9697 at 0°. It has no sensible action on polarised light.

Ethylic isobutyrate boils at 113° under the normal pressure, and methylic isobutyrate at 93°. The former has a density of 0·890 at 0°, and the latter one of ·9056 at the same temperature.

C. E. G.

Valeric Acid. By I. PIERRE and E. PUCHOT (Compt. rend., lxxv, 1005—1006.

VALERIC acid produced by the oxidation of amylic alcohol, contains a molecule of water which cannot be removed by simple distillation. It boils at 178° under the pressure of 760 mm., and has a density of ·9470 at 0°. It rotates the plane of polarisation in the same direction as crystallised sugar. Both amylic and butylic valerate rotate the plane of polarisation in the same direction, the former more than, and the latter less than the acid itself.

C. E. G.

Heptylic Acid from the Hexyl Alcohol of Heracleum Oil. By A. FRANCHIMONT (Deut. Chem. Ges. Ber., v, 786—788).

THE author has converted the (probably normal) hexyl alcohol from Heracleum oil (this Journal, 1872, 161), into the corresponding acid of the acetic series containing seven atoms of carbon, by the usual method.

The heptylic acid obtained is at ordinary temperatures a colourless oily liquid, which boils at 223°—224° under a pressure of 762·7 mm. of mercury at 0°, the thermometer being entirely immersed in the vapour.

It solidifies in a mixture of ice and salt, but entirely liquefies again at $-8°$. Its specific gravity is ·9212 at 24°.

The ethylic ether is a colourless liquid of pleasant fruity odour; specific gravity, ·874 at 24°; boiling point, 187°—188° under a pressure of 761·13 mm. of mercury at 0°, the thermometer being entirely immersed in the vapour. It does not solidify at $-18°$.

The sodium, barium, calcium, zinc, cadmium, lead, copper, and silver salts are described at length.

The evidence is not sufficient to enable us to decide whether the acid so prepared is identical or not with that obtained from normal heptane by Schorlemmer, since the latter has stated scarcely any of the properties of his acid.

The author refers to the fact that the zinc and cadmium salts of heptylic and nonylic acid have exactly the same melting point; the melting point therefore affords no criterion of purity. He states also that if regard be had to the specific gravities of the normal fatty acids, from butyric on to nonylic acid, these being taken either at the same temperature or within such limits that the correction does not affect the second decimal, it will be noticed that there appears to be a difference of about one unit in the second decimals between every two next homologous acids, whilst the difference between butyric and propionic acids already amounts to four, between propionic and acetic acids to about six, and between acetic and formic acids to a still greater number of units.

H. E. A.

Ethyl Fumarate. By A. LAUBENHEIMER (Ann. Chem. Pharm., clxiv, 294)

FUMARIC acid is readily etherised by absolute alcohol at 120°, *ethyl-fumaric acid*, $C_4H_2O_2\left\{\begin{matrix}OC_2H_5\\OH\end{matrix}\right.$, being thereby produced. This may be obtained by diluting the alcoholic solution with water, when the ether separates, and can be obtained pure by recrystallisation from alcohol, or, better, by neutralisation of the liquid with sodium carbonate and precipitation with silver nitrate. Silver fumarate is insoluble in boiling water, while silver-ethyl fumarate dissolves in hot water, separating in needles as the solution cools. From this salt the acid is obtainable by treatment with sulphuretted hydrogen.

Larger quantities of ethyl-fumaric acid may be procured by Hagen's process, viz., passing hydrogen chloride into a boiling solution of malic acid in absolute alcohol. The acid is sensibly volatile with alcohol vapour. Maleic acid is simultaneously found.

Attempts to procure ethyl-fumaric acid by partial saponification of diethylfumarate proved fruitless, half the ether being unattacked, while the other half was wholly decomposed, giving fumarate. Silver-ethyl fumarate is soluble in 436 parts of water at 8·9°, and in 331 parts at 12·1°.

Diethyl fumarate, $C_4H_2(C_2H_5)_2O_4$, prepared by Hagen's process, was found to boil at 218° under a pressure of 745·7° mm. (Hagen gives 225° as the boiling point.)

C. R. A. W.

Observations on the so-called Anhydrides of Lactic Acid.

By J. WISLICENUS (Ann. Chem. Pharm., clxiv, 181—196).

1. *Dehydration of Lactic Acid at Ordinary Temperatures.*—On allowing a quantity of the pure aqueous acid to remain several months over sulphuric acid *in vacuo*, the amount of acid present being determined from time to time by titration with normal soda-solution, it was noticed that, notwithstanding the loss in weight which occurred, the amount of alkali required became continuously less and less, so that evidently the lactic acid had been converted by a process of dissociation into the anhydride.*

The author therefore examined by titration a number of preparations of lactic acid kept for different intervals of time over sulphuric acid, and from the discussion of the results has come to the following conclusions:—

(1.) That the first anhydride is already present, together with the acid, before the whole of the water has evaporated from the solution, the proportion of the anhydride increasing as the amount of water present diminishes. A pure lactic acid of the formula $C_3H_6O_3$ is therefore not obtainable.

(2.) That not only does the first etherification, in consequence of the continuous withdrawal of water, increase when lactic acid is preserved in a perfectly dry atmosphere at ordinary temperatures, but that the second phase of the process, viz., the continuation of etherification or formation of lactide also takes place, and likewise in a proportion which increases with the time of exposure.

In a future communication the author proposes to bring forward evidence which renders it highly probable that the lactic acids unite with water to form hydrates similar in constitution to those yielded by formic, acetic, and valerianic acids, and he expresses his belief that a dilute aqueous solution of a lactic acid has the composition—

$$v\mathrm{H_2O} + w\left\{\begin{matrix}\mathrm{C_nH_{2n}.OH}\\ \mathrm{C(OH)_3}\end{matrix}\right. + x\left\{\begin{matrix}\mathrm{C_nH_{2n}.OH.}\\ \mathrm{CO.OH.}\end{matrix}\right.$$

2. *Dehydration of Lactic Acid at Higher Temperatures.*—The dissociation naturally takes place far more rapidly under these conditions. Observations quoted in this part of the communication fully prove that lactide can exist for many days in presence of water and lactic acid without becoming entirely converted into the first anhydride.

3. *Note on Salts of the so-called Lactic Anhydride.*—The formation of magnesium and potassium salts of the so-called anhydride is referred to. The numbers obtained on analysis of the latter—an amorphous viscid mass—are given.

* In a previous communication (*Ann. Chem. Pharm.*, cxxxiii, 258) the author has called attention to the fact that the first anhydride of lactic acid is formed from two molecules of lactic acid, the one acting as acid, the other as alcohol, so that it is in reality a monobasic acid:—

$$\begin{matrix}\mathrm{CH_3}\\ \mathrm{CH.OH}\\ \mathrm{CO.OH}\end{matrix} + \begin{matrix}\mathrm{CH_3}\\ \mathrm{CH.OH}\\ \mathrm{CO.OH}\end{matrix} = \mathrm{H_2O} + \begin{matrix}\mathrm{CH_3} & \\ \mathrm{CH.OH} & \mathrm{CH_3}\\ \mathrm{CO.O} & \!\!\!\text{——}\mathrm{CH}\\ & \mathrm{CO.OH.}\end{matrix}$$

4. *Action of Water on the so-called Lactic Anhydride*—The conversion of this body into lactic acid by water at ordinary temperatures appears to take place with extreme slowness. 5 grms. of a dehydrated product containing 89·86 per cent. of "anhydride" and 10·16 per cent. of lactide, were dissolved about six months ago in about 10 c.c. of absolute alcohol, and precipitated by 50 c.c. of water. The viscid precipitate, although considerably diminished, has not yet disappeared.

H. E. A.

Condensation-products of Aldehydes. By A. Borodin (Deut. Chem. Ges. Ber., v, 480—482).

In 1864 the author has already shown that by the action of sodium on valeral no sodium-valeral is produced, but that valeric acid, amyl alcohol, a new alcohol, $C_{10}H_{22}O$, and other products, are formed. He has now studied this reaction more fully, and finds that first water is eliminated, and the aldehyde $C_{10}H_{18}O$ is produced, together with a high boiling polymeride. This aldehyde, which has also been obtained by Kekulé and Riban, is an oily liquid, boiling at 195°, and possessing a strong aromatic smell. It combines with sodium bisulphite, and yields on oxidation the acid $C_{10}H_{18}O_2$, formerly described as isocapric acid. By nascent hydrogen it is converted into the alcohol $C_{10}H_{22}O$, whilst caustic soda acts on another portion of the valeral, converting it into a polymeric modification, a viscid oily liquid which does not combine with sodium bisulphite, and which on distillation is again converted into valeral. The same compound is obtained pure by the action of solid caustic potash at 0°. By abstraction of water it yields the compound $C_{20}H_{38}O_3$, an oily liquid boiling between 260° and 290°, which when heated with alkalis is resolved into valerianic acid, amyl alcohol, and some valeral. The same products are formed by the action, at a high temperature, of alkalis, zinc chloride, and hydrochloric acid on valeral.

Similar compounds may be obtained from œnanthol. By acting on it in the cold with solid caustic potash, it is converted into two polymeric modifications, one a crystalline solid, and the other an oily liquid. Both yield on distillation œnanthol and condensation-products, with the abstraction of water.

By acting with hydrochloric acid on acetaldehyde a condensation product was obtained resembling that described by Wurtz. But whilst the latter is resolved by distillation into water and crotonic aldehyde, that prepared by the author yielded principally acetaldehyde.

C. S.

Action of Aldehyde on Acetamide. By N. Tawildarow (Deut. Chem. Ges. Ber., v, 477).

By heating these compounds together in sealed tubes the body, $CH_3CH(NH.C_2H_3O)_2$, is formed, crystallising in large prisms, melting at 169°, and distilling with partial decomposition. By the action of acids aldehyde is set free again.

C. S.

Acediamine. By N. TAWILDAROW (Deut. Chem. Ges. Ber., v, 477).

ACCORDING to Strecker, the hydrochloride of this base is produced by acting with hydrochloric acid gas on fused acetamide, but on repeating this experiment the author obtained only a mixture of diacetamide and ammonium chloride; neither did he succeed in obtaining it by the action of ammonium chloride on acetamide, or by that of ammonia or ammonium iodide on acetonitrile. C. S.

Cyanogen Derivatives of Acetone. By F. URECH (Ann. Chem. Pharm., clxiv, 255—279).

DURING the course of a series of experiments made in order to ascertain the best method of preparing acetonic acid, several new derivatives of acetone were discovered.

The vapour of dry hydrocyanic acid was passed into acetone which was kept cool, and the product, after remaining for some time, was distilled, the greater part passing over at 120°. This substance the author considers to be *acetone-cyanhydrin*, formed by the direct addition of hydrocyanic acid to acetone.

$$\begin{array}{l} CH_3 \\ | \\ CO + HCN \\ | \\ CH_3 \end{array} = \begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ HO—C—CN \\ \quad\quad | \\ \quad\quad CH_3 \end{array}$$

Acetone-cyanhydrin is a very unstable compound, the addition of silver nitrate giving rise to the formation of silver cyanide and the liberation of acetone. By allowing a portion of the acetone which had been saturated with hydrocyanic acid to remain for some months, heating it in a sealed tube to 100°, and allowing the more volatile portions to evaporate spontaneously, a yellow syrup was obtained which yielded ammonia and acetonic acid when boiled with a dilute mineral acid; when, however, the heating in a sealed tube was much prolonged, a brown mass was obtained which no longer yielded acetonic acid. The action of alkalies on it gave rise to ammonia; the formation of a small quantity of a substance crystallising from water in efflorescent prisms was noticed at the same time.

The action of nascent hydrocyanic acid on acetone was studied by covering slightly moist pure potassium cyanide with acetone, and adding excess of aqueous hydrochloric acid, or passing in this acid in the state of gas. The brown mass thus produced was separated from the liquid and exhausted with ether. The residue left on evaporating the ethereal solution gave, when dissolved in water and neutralized with zinc carbonate, an abundant crop of zinc acetonate:

$$\begin{array}{l} CH_3 \\ | \\ CO + KCN + 2HCl + 2H_2O \\ | \\ CH_3 \end{array} = \begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ HO—C—CO.OH + KCl + NH_4Cl. \\ \quad\quad | \\ \quad\quad CH_3 \end{array}$$

When, however, for each molecule of potassium cyanide present, only one molecule of hydrochloric acid is added, the ethereal solution of the product deposits on evaporation a crystalline substance which is not acid. Analysis led to the formula, $C_7H_{13}NO_2$.

$$2\begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + KCN + HCl = KCl + HO-\begin{array}{c}H_3C\\|\\C\\|\\CH_3\end{array}-O-\begin{array}{c}CH_3\\|\\C\\|\\CH_3\end{array}-CN$$

Diacetonecyanhydrin, the product thus obtained, is easily soluble in water, alcohol, and ether, and crystallises from these solvents in thick shining anhydrous prisms. It melts between 135° and 152°, and sublimes below its melting point in long, colourless needles. It is decomposed at the ordinary temperature by hydrochloric acid into ammonium chloride, acetone, and acetonic acid.

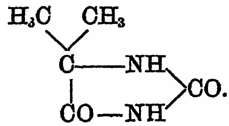
$$HO-\begin{array}{c}CH_3\\|\\C\\|\\CH_3\end{array}-O-\begin{array}{c}CH_3\\|\\C\\|\\CH_3\end{array}-CN + HCl + 2H_2O = \begin{array}{c}CH_3\\|\\CO\\|\\CH_3\end{array} + HO-\begin{array}{c}CH_3\\|\\C\\|\\CH_3\end{array}-CO-OH + NH_4Cl$$

If the products of this reaction be distilled, a distillate is obtained consisting principally of acetone. This was treated with quick lime to remove free acid and water, and the acetone was separated by distillation. In the residue there was found a body crystallising in prismatic crystals, and containing the elements of calcium chloride with two molecules of monacetonecyanhydrin, $CaCl_2 + 2C_4H_7NO$.

An attempt to form this substance by the addition of calcium chloride to the ethereal solution of the crude product obtained by the action of hydrochloric acid on acetone and potassium cyanide, led to the formation of a compound of diacetonecyanhydrin and calcium chloride, $CaCl_2 . C_7H_{13}NO_2 . 5H_2O$, a substance which separated from its ethereal solution in large crystals. When dried at 100° it contains $CaCl_2 . C_7H_{13}NO_2 . H_2O$.

The author considers that the compound of hydrocyanic acid and acetone above described is analogous to Volkel's hydrocyanate of benzoyl hydride, and that the splitting up of diacetonecyanhydrin under the influence of hydrochloric acid is analogous to that of amygdalin when subjected to the action of the same reagent.

Hydrochloric acid was added to commercial potassium cyanide (containing cyanate) covered with acetone, and after the termination of the reaction the liquid was poured off from the deposited salts and evaporated, whereupon it yielded crystals of potassium chloride mixed with long prisms. These prisms, after crystallisation from ether and sublimation, gave numbers corresponding with the formula $C_5H_6N_2O_2$. This compound, formed by the conjunction of single molecules of acetone, hydrocyanic acid, and cyanic acid, is regarded by the author as *acetonyl-urea*—

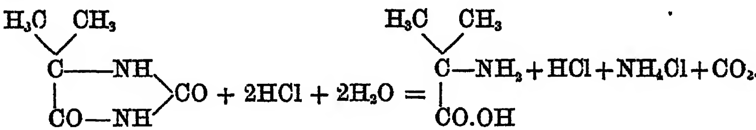


or as *dimethyl-hydantoin.*

Acetonyl-urea is easily soluble in water, alcohol, and ether, and separates from these solvents in large glistening prisms. It has a peculiar bitterish taste and melts at 175°, at the same time subliming in long needles. With silver nitrate it forms the compound $C_6H_4N_2O_2 . AgNO_3$, which crystallises in long prisms, easily soluble in water, and exploding when rapidly heated.

By warming a solution of acetonyl-urea with silver oxide, a white powder was produced, which, when purified by solution in ammonia and precipitation by acetic acid, gave numbers corresponding with *argento-acetonyl-urea*, $C_6H_7AgN_2O_2$. When acetonyl-urea is boiled with baryta-water, the solution, after the separation of the excess of baryta and acetonyl-urea, yields a barium salt having the composition $(C_5H_8N_2O_3)_2Ba(OH)_2$, or that of the barium salt of an acetonuraminic acid. The free acid is so unstable that when it is liberated by sulphuric acid and the solution is agitated with ether, the ethereal solution yields acetonyl-urea on evaporation.

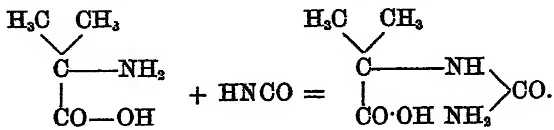
Acetonyl-urea, when heated with hydrochloric acid to 150°—160°, splits up into carbonic anhydride, sal-ammoniac, and α-amido-isobutyric acid—



The α-amidoisobutyric acid thus obtained exhibits the characteristic properties of the glycocines. *Cupro-alphamidoisobutyric acid*, $(C_4H_8NO_2)_2Cu$ forms violet-blue crystals, easily soluble in water. *Argento-alphamidoisobutyric acid*, $C_4H_8NO_2Ag$, crystallises in silky needles, soluble in water.

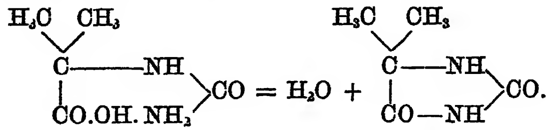
By evaporating to dryness the product of the action of hydrochloric acid on acetonyl-urea, and exhausting the residue with spirit, there was obtained a *hydrochloride of alph-amidoisobutyric acid*, $C_4H_9NO_2HCl + H_2O$. It crystallises in short, colourless prisms, exhibits a strong acid reaction, is very soluble in water, moderately soluble in alcohol, and insoluble in ether. When its solution is evaporated with platinum chloride, crystalline masses corresponding with platinochloride of alanine are deposited. When it is treated with solution of potassium nitrite, acetonic acid is formed, nitrogen being set free at the same time.

Synthesis of Acetonyl-urea from the Products of its Decomposition.—An aqueous solution of sulphate of alphamidoisobutyric acid was evaporated with potassium cyanate. The residue, on being exhausted with alcohol, evaporated, and treated with sulphuric acid, yielded *acetonyl-uramic acid* or *alph-uramidoisobutyric acid.*



This compound is moderately soluble in hot water and alcohol, but insoluble in ether. It melts and gives off water at 160°. *Silver salt*, $C_5H_9N_2O_3Ag$: tufts of needles, slightly soluble in water.

Acetonyluramic acid, when heated for a long time to 130°—140°, evolves water and yields acetonyl-urea.



The author is engaged in extending his investigations to other ketones and to the aldehydes.

T. B.

Action of Sodium on Crystalline Dibromobenzene. By F. Riese* (Ann. Chem. Pharm., clxiv, 161—176).

About twice the weight of sodium necessary for the complete removal of the bromine from the quantity of dibromobenzene employed was added to anhydrous ether and heated with it until hydrogen ceased to be evolved, and after cooling, the dry crystalline dibromobenzene was introduced. Action set in only after the mixture had been heated for some hours on the water-bath; it was then evidenced by the appearance of small black points on the sodium; and without exterior application of heat, the mixture continued to boil gently until finally after 5—7 hours the sodium was entirely covered by a loose green-black mass. The product was exhausted with ether, but it was found that the substance left on distilling off the ether was for the greater part decomposed on distillation, and also that it contained a considerable quantity of bromine.†

On mixing the ethereal extract with much alcohol, a yellow-brown amorphous mass separated; the supernatant liquid gave a moss-like crystallisation on evaporation, of which, however, only a portion was redissolved by alcohol; and by repeating the treatment with alcohol, &c., several times, the product could be separated into two portions:

* This and the following notice on β-dibromobenzene were the subject of the author's inaugural dissertation published at Easter, 1869; but the experiments were then only briefly described in the Berlin Chemical Society's Journal, and the Zeitschrift fur Chemie.

† Attempts to remove the whole of the bromine by modifications of the mode of treatment were unsuccessful. Thus, sodium was without action on a solution of dibromobenzene in benzene; on fusing dibromobenzene with sodium, so energetic a reaction took place that the whole became carbonised; finely divided silver was also without action on dibromobenzene at its boiling point.

the one easily soluble in alcohol and containing little bromine; the other insoluble and containing much bromine. Both of these gave distillates which crystallised on cooling, but that from the latter was much decomposed on heating.

On submitting the mixed product to distillation in a current of steam, a white crystalline body passed over, which proved to be diphenyl, $C_{12}H_{10}$; a relatively small quantity was obtained, however. The residue, after removal of the diphenyl, was distilled, and although much of it underwent decomposition, a crystalline substance was separated and purified by repeated distillation, washing with ligroïn, and final recrystallisation from benzene. The numbers obtained on analysis lead to the formula C_9H_7, or $C_{18}H_{14}$, which is that of *diphenyl benzene*, $C_6H_4(C_6H_5)_2$, and since a body of identical properties was obtained in considerable quantity by the action of sodium on a mixture of mono- and di-bromobenzene, there can be little doubt that such is its nature.

Diphenylbenzene melts at 205°, and boils probably at about 400°; in the pure state it is insoluble in alcohol, but dissolves easily in hot benzene, from which it separates on cooling in small, flat, white needles.

But the main product of the reaction does not consist of either of these bodies, but of the above-mentioned brownish amorphous brominated substance, scarcely soluble in alcohol and ether, although easily soluble in benzene and carbon bisulphide, from which it is again precipitated in the amorphous state on addition of the two former liquids. A product thus purified was found by analysis to contain 77·49 per cent. of carbon, 4·07 per cent. of hydrogen, and 17·68 per cent. of bromine.

The author gives the following equation as perhaps representing the course of the reaction:—

$$25C_6H_4Br_2 + 23Na_2 = 4C_{30}H_{19}Br + C_6H_4(C_6H_5)_2 + C_{12}H_{10} + 46NaBr.$$

The formula $C_{30}H_{19}Br$ is that of a monobrominated pentaphenylene, and such a substance would contain 78·43 per cent. of carbon, 4·14 per cent. of hydrogen, and 17·43 per cent. of bromine, numbers which differ only slightly from those obtained on analysis of the amorphous product. As a matter of fact, also the relative proportions of the products obtained accord fairly, as far as could be judged, with those required by the equation above given.

H. E. A.

On β-Dibromobenzene. By F. Riese (Ann. Chem. Pharm., clxiv, 176—180).

To prepare the dibromobenzene for the above experiments, Riche and Bérard's method was employed, which consists in heating a mixture of one part of benzene and eight parts of bromine to boiling during 36—48 hours. The author noticed that the crystalline α-dibromobenzene*

* The author found distillation in a current of steam the best mode of purifying α-dibromobenzene, the distillate being subsequently once recrystallised from boiling alcohol.

thus obtained was saturated with an oily liquid from which it could be separated by pressure. The proportion of oil formed was about one-fifteenth of the weight of the crystalline dibromobenzene obtained simultaneously. On distillation it was partially decomposed, with evolution of hydrobromic acid; it was therefore digested with alcoholic potash, &c., whereby the volume was only slightly reduced, but after this treatment it could be distilled unchanged, the greater portion boiling between 209°—211° (corr. 213°—215°).

This β-dibromobenzene is a colourless, mobile, strongly refracting liquid, miscible in all proportions with ether and benzene, and moderately soluble even in cold alcohol; carefully cooled to − 27° it did not solidify, but immediately became solid when touched with a glass rod; the solid melts at − 1°.

It dissolves in the strongest fuming nitric acid with perceptible evolution of heat, and is converted into *nitro*-β-dibromobenzene, which crystallises in pale yellow needles melting at 58° and boiling at 296°. (The isomeric body from α-dibromobenzene melts at 84°).

H. E. A.

Amidazobenzene. By G. Schmidt (Deut. Chem. Ges. Ber., v, 480).

Nitroazobenzene reduced with ammonium sulphide, yields an amidazobenzene, identical with that produced from the isomeric diazamidobenzene by a molecular change.

C. S.

The Oxidation of Camphor Cymene in the Animal Organism. By Nencki and Ziegler (Deut. Chem. Ges. Ber., v, 749—751).

Commercial camphor-cymene was found, when fractionated by Linnemann's method, to yield a portion boiling at 173°, the oxidation of which gave rise to terephthalic acid with a small proportion of toluic acid. This cymene was administered first to dogs, and afterwards to men, in doses of three grams daily. The urine of those to whom the cymene had been administered, was found to contain an acid having the composition $C_{10}H_{12}O_2$. This acid crystallises from water in small white needles, sublimes unchanged, and melts at 115°. It is easily soluble in alcohol, ether, and glacial acetic acid, and but very slightly soluble in water. Its salts, when subjected to dry distillation, yield a hydrocarbon having an odour like that of cumin oil. No compound of this acid with glycocine was recognised.

The author regards this acid as the propylbenzoic acid $C_6H_4\left\langle\begin{matrix}C_3H_7\\COHO\end{matrix}\right.$; corresponding to the terephthalic acid series, or as toluol-propionic acid, $C_6H_4\left\langle\begin{matrix}CH_2CH_2COOH\\CH_3\end{matrix}\right.$; and he considers that it is identical with the acid obtained from cumin aldehyde by Gerhardt and Cahours.

T. B.

Occurrence of Benzyl Alcohol in Liquid Storax. By A. Laubenheimer (Ann. Chem. Pharm., clxiv, 289).

Previous experimenters have found in liquid storax, *styrolene* C_8H_8, *cinnamic acid*, $C_9H_8O_2$, and *styracin* (cinnyl cinnamate) $C_9H_7(C_9H_9)O_2$. A product obtained by saponifying impure styracin was found to begin to boil at a little above 100°, various fractions being collected by distillation in hydrogen.

The fraction at 205°—207° had the composition of *benzyl alcohol*, C_7H_8O, and gave benzoic aldehyde and apparently benzoic acid (melting at 119° after several sublimations) by oxidation with potassium dichromate and sulphuric acid.

The fraction at 217° had the composition of *xylyl alcohol*, $C_8H_{10}O$.

The fractions at 230°, 231°, 233°—243°, 243°—244°, had the composition of the unknown alcohol, $C_9H_{12}O$, but the existence of this body is not demonstrated clearly.

The fraction at 250° consisted of *styrone* (cinnamic alcohol). Simon finds that styrone boils at 220°; Scharling at 230°; E. Kopp at 254°; and Wolff at 250°.

Besides these, there were obtained a small quantity of distillate below 200°, which appeared to be a mixture of hydrocarbons and oxidised bodies; and a small quantity of substance boiling up to 260° with visible decomposition.

C. R. A. W.

(Meta ?)-Chlorophenol and its Nitro-Derivatives. By A. Faust and H. Müller (Deut. Chem. Ges. Ber., v, 777—779).

The first product of the action of chlorine on phenol is a mixture of two isomeric monochlorophenols, but hitherto only one of these had been obtained in the pure state; the authors have now succeeded, however, in isolating the second.

Dry chlorine was passed into 500 grms. of pure fused phenol until the weight was increased 200 grams; the product, which boiled between 175° and 220°, was then distilled, and the portion boiling at 175°—200°, collected apart and carefully fractioned. The new monochlorophenol thus obtained is a clear colourless liquid, boiling at 175·5°—177°; it did not solidify at −15°, and possessed the peculiar unpleasant, persistent odour characteristic of the chlorophenols.

The same body was obtained by distillation of the platinum double salt of the diazo-compound from volatile nitrophenol; hence it is probably metachlorophenol, since volatile nitrophenol is generally regarded as belonging to the meta-series.

On nitration by acid of 1·36 sp. gr., diluted with an equal volume of water, it yields two isomeric mononitrochlorophenols, one of which is identical with orthonitrochlorophenol, the body produced by chlorinating non-volatile nitrophenol, &c.; the other is new. This latter chloronitrophenol melts at 70°; it is only slightly soluble in water, and separates from the hot aqueous solution, partly as oil, partly in fine, yellow needles; it has a strong saffron-like odour, and is extremely volatile with vapour of water. The potassium, calcium, barium and

silver derivatives are described; these are either red or red-brown in colour, and excepting the first, are difficultly soluble in water.

On nitration by acid of 1·36 sp. gr., the new chlorophenol yields, as sole product, a dinitrochlorophenol, melting at 111°*, and identical with Faust and Saame's β-dinitrochlorophenol, and with the product of the action of chlorine on ordinary α-dinitrophenol, &c.

H. E. A.

Diphthalyl. By E. Ador (Ann. Chem. Pharm., clxiv, 229—254).

The chloride of phthalic acid is readily obtained by boiling gently for several days a mixture of one molecule of phthalic acid and two molecules of phosphorus pentachloride to which a little oxychloride is added. As soon as the evolution of hydrochloric acid ceases, the product is distilled from an oil-bath, and the chloride boiling at 270° is collected separately. It is a yellowish oily liquid, which is heavier than water, and only slowly decomposed by it. When exposed to moist air, it is gradually converted in beautiful clinorhombic crystals of phthalic anhydride, boiling at 275°.

Phthalyl chloride is very readily acted upon by silver dust; by gradually adding 14 parts of the latter to 10 parts of the chloride, a solid mass was obtained, which, in order to finish the reaction, was heated for some time in an oil-bath to 150°. The products of the reaction consist of phthalic anhydride, a portion of which sublimes during the latter operation, a resinous body soluble in alcohol, and *diphthalyl*, $C_{16}H_8O_4$, which is isolated by exhausting the product repeatedly with boiling water and with alcohol. The dried residue is then heated in a combustion-tube, through which a slow current of dry carbon dioxide passes, the diphthalyl subliming as a light, orange-coloured crystalline mass, which may be purified by dissolving it several times in hot phenol, and reprecipitating it by alcohol. The pure com-

* This observation of F. and M. proves the correctness of my conclusion (this Journal [2], x, 96), that the dinitrochlorophenol (melting at 103°) which Griess obtained by nitration of a crude chlorophenol prepared by passing a moderately rapid stream of chlorine into 1 lb. of phenol during fifteen hours, is not identical with Stenhouse's dinitrochlorophenol (melting at 103°), but with the isomeride melting at 110°—111°, the low melting point observed by Griess being doubtless due to the presence of an isomeride of lower melting point.

It is a remarkable fact, but, according to my observations, on chlorinating phenol, almost the whole, if not the whole, of the latter is converted into the monochlorinated derivative before the formation of dichlorophenol begins. This is of importance, because it has been assumed that Griess's chlorinated phenol was a mixture of mono-, di-, and perhaps even contained trichlorophenol, which, however, was certainly not the case; for Mr. Griess informs me that he did not observe the formation of the dichloronitrophenol melting at 121·5°, which is the characteristic nitration-product of ordinary dichlorophenol, and which, on account of the highly characteristic appearance of its metallic derivatives, could not have escaped detection had it been formed. I may add that the method of purification adopted by Griess, namely, solution in ammonia, &c., was the very best that could have been employed to effect the separation of the dinitrochlorophenol melting at 110°—111° from the isomeride melting at 80·5°, the characteristic nitration-product of ordinary monochlorophenol—since the ammonium derivative of the former is exceedingly insoluble in cold water, whilst that of the latter is readily soluble.—H. E. A.

pound has a pale yellow colour; it is insoluble in water, scarcely soluble in alcohol and ether, sparingly soluble in chloroform, carbon disulphide, and liquid hydrocarbons. Phenol and cold concentrated sulphuric acid, are the only liquids which dissolve larger quantities of it. It melts a little above 300°, subliming at the same time in soft felted needles. The formation of diphthalyl is explained by the equation:

$$2C_6H_4\left\langle\begin{matrix}COCl\\ COCl\end{matrix}\right. + 2Ag_2 = 4AgCl + C_6H_4\left\langle\begin{matrix}CO-CO\\ CO-CO\end{matrix}\right\rangle C_6H_4.$$

When diphthalyl is heated in a current of air, a sublimate is obtained, consisting of phthalic anhydride, a red resinous body, and unaltered diphthalyl.

Diphthalylaldehydic acid, $C_{16}H_{10}O_5$, is produced by dissolving diphthalyl in hot caustic alkalis; on the addition of hydrochloric acid to the solution, a bulky precipitate of the new acid is obtained. After drying it is a white, voluminous, indistinctly crystalline powder; it is insoluble in water, very sparingly soluble in alcohol, ether, chloroform, petroleum-naphtha, and benzene, but dissolves readily in hot phenol, cold caustic soda, and solutions of alkaline carbonates.

When rapidly heated it melts only above 300°, but on heating it for six hours to 180°, it becomes perfectly liquid, and then consists of a mixture of phthalic acid, a little diphthalyl, and an acid which has the composition $C_{16}H_{10}O_3$, and melts between 200° and 225°.

Neither the free acid nor any of its salts could be obtained in the pure state; the solutions of the latter soon deposit microscopic needles of diphthalyl; this decomposition takes place quickly on heating, and the yield is the larger the better the air has been excluded, whilst in contact with air much less diphthalyl is obtained. On adding hydrochloric acid to the remaining solution, a mixture of two acids is precipitated; one of them appears to be identical with the acid $C_{16}H_{10}O_3$; it is soluble in absolute alcohol and a large quantity of boiling water, from which it crystallises in prisms; the second acid, which is much less soluble in alcohol, is *diphthalic acid*, $C_{16}H_{10}O_6$, and is also formed by boiling the sodium salt of diphthalylaldehydic acid with silver nitrate, and by heating diphthalyl with concentrated nitric acid.

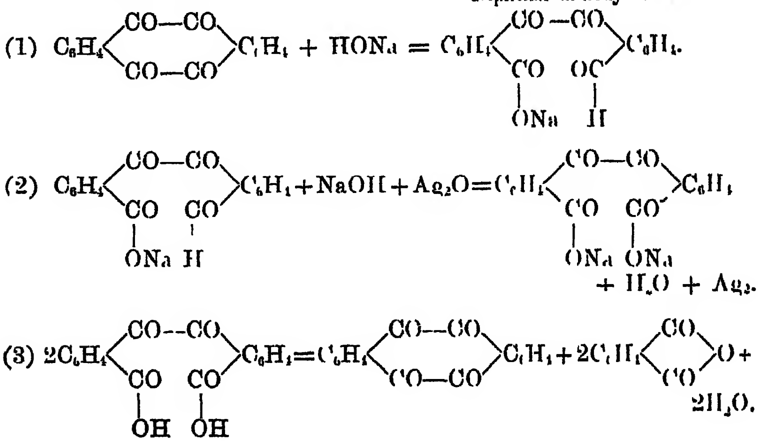
Diphthalic acid forms microscopic needles or plates; it is almost insoluble in water, alcohol, and ether, sparingly in chloroform, carbon disulphide, and ether, but readily in solutions of the caustic alkalis and their carbonates and in phenol. It melts at 265°.

Barium diphthalate, $C_{16}H_8BaO_6 + 2H_2O$, crystallises in small colourless plates. *Silver diphthalate*, $C_{16}H_8Ag_2O_6$, crystallises from boiling water in small needles. A zinc-salt of a constant composition could not be obtained; the salts of the alkali-metals are very deliquescent, and form indistinct crystals; the copper-salt is a bulky, bluish-white precipitate, and the lead-salt a dense white precipitate. It is very difficult to obtain diphthalic acid and its salts perfectly pure, as they readily absorb oxygen. By boiling their alkaline solution, even in closed vessels, resinous acids and phthalic acid are formed, whilst when the operation is performed in open vessels, only the latter acid is produced. Phthalic acid is also formed by heating diphthalic acid for some time,

with nitric acid, and, together with diphthalyl and phthalic anhydride, when diphthalic acid is heated a few degrees above its melting point.

The formation and constitution of diphthalylaldehydic acid and diphthalic acid, and the decomposition of the latter by heat may be explained as follows.—

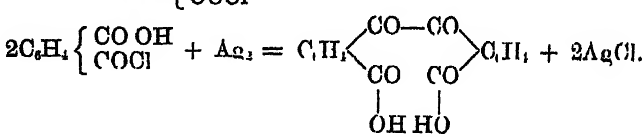
Diphthalylaldehydic acid



Dichlorodiphthalyl, $C_{16}H_6Cl_2O_4$, is produced by heating diphthalyl with phosphorus pentachloride and some oxychloride in sealed tubes for five hours to 160°. It crystallises from hot benzene in rhombic plates, melting at 248°, and solidifying again at 196°. It is almost insoluble in alcohol, but readily soluble in alcoholic potash, with formation of potassium chloride, and a compound crystallising in hexagonal plates, probably a dioxydiphthalyl.

Diphthalyl dissolves in cold bromine, apparently without change, but on heating the mixture, hydrobromic acid is given off, and *monobromodiphthalyl*, $C_{16}H_7BrO_4$, is formed, together with a compound containing more bromine. Monobromodiphthalyl is easily obtained pure by heating diphthalyl with bromine and water in sealed tubes to 100°. It is soluble in benzene, and crystallises in small hexagonal plates.

The bye-products obtained in the preparation of diphthalyl always contain diphthalic acid; the formation of this acid may be explained by assuming that the phthalic chloride used contained some phthalic monochloride, $C_6H_4\left\{\begin{matrix}CO.OH\\COCl\end{matrix}\right.$.



In order to obtain this monochloride, phthalic anhydride was heated with somewhat less than one molecule of phosphorus pentachloride. The product consisted of unaltered phthalic anhydride or phthalic dichloride,

and the compound $C_{16}H_6Cl_8O_6$, probably a combination of $C_6H_4\left\{\begin{matrix}COCl\\COCl\end{matrix}\right.$ with $C_6H_4\left\{\begin{matrix}CO.OH\\CO.Cl\end{matrix}\right.$. It crystallises in long plates, melting at 17°. On heating it with silver-dust, it yields, besides phthalic anhydride and diphthalyl, a considerable quantity of diphthalic acid.

The resinous bye-products contain, besides diphthalic acid, several other compounds; of these, one having the composition $C_{16}H_{10}O_4$ crystallises from boiling water in small white needles, melting at 240°, with formation of phthalic anhydride. It is soluble in ammonia; silver nitrate produces in the neutral solution a white precipitate, having the composition $C_{16}H_{10}Ag_2O_5$; the corresponding barium salt is obtained by dissolving the acid in baryta water, and evaporating the solution *in vacuo*. It crystallises in small plates, having the composition, $C_{16}H_{10}BaO_5 + H_2O$. When the ammonium salt is boiled with silver nitrate, reduction takes place, and a compound having the properties diphthalic acid is formed. The compound $C_{16}H_{10}O_4$ is therefore an anhydride, either $C_6H_4\left\{\begin{matrix}CO - CO\\CH_2\ O.CO\end{matrix}\right\}C_6H_4$, or $C_6H_4\left\{\begin{matrix}CH_2 - CO\\CO.O.CO\end{matrix}\right\}C_6H_4$, which is probably formed by the action of diphthalic acid on diphthalyl:

$$C_{16}H_{10}O_6 + C_{16}H_8O_4 = C_{16}H_{10}O_4 + 2C_8H_4O_3.$$

C. S.

Trinitronaphthalenes. By BEILSTEIN and KÜHLBERG (Deut. Chem. Ges. Ber., v., 480).

BY acting with a mixture of nitric acid and sulphuric acid on dinitronaphthalene, melting at 212°, two isomeric trinitro-compounds are formed. One melting at 208° is probably identical with Laurent's trinitronaphthalene; the other melts at 147°.

C. S.

Derivatives of Naphthalene Tetrachloride. By E. GRIMAUX (Bull. Soc. Chim. [2], xviii, 205—212).

Dichloronaphthydrene glycol*, $C_{10}H_8Cl_2(OH)_2$.—This compound is produced when naphthalene tetrachloride (melting at 180°) is heated with 80 parts of water for some hours to 180°–190°, or boiled with water for some days. On concentrating the solution, the glycol separates in brownish crystals, which become colourless by treatment with animal charcoal. From ether it crystallises in large, hard, but ill-defined prisms. By heating it with acetyl chloride, it is converted into the *diacetate*, $C_{10}H_8Cl_2(OC_2H_3O)_2$, crystallising from ether in hard short prisms, melting at 130°—131°. The *dibenzoate*, $C_{10}H_8Cl_2(OC_7H_5O)_2$, obtained by the action of benzoyl chloride on the glycol, is insoluble in water, and soluble in alcohol and ether. It forms small white crystals. On distilling the glycol with hydrochloric or hydrobromic acid, a portion is transformed into a black matter, whilst with the aqueous vapour needles of *monochloronaphthol*, $C_{10}H_6Cl.OH$, distil over. This com-

* Napthydrene is the name given by the author to dihydronaphthalene.

pound is only sparingly soluble in cold water, a little more in boiling water, and crystallises in long, fine, exceedingly light needles, melting at 109°, and emitting the odour of the phenols. Its aqueous solution reddens slightly in the air. It gives no colours with ferric chloride or chloride of lime. Like other phenols, it dissolves in alkalis, and is reprecipitated by acids. On dissolving it at a gentle heat in a little sulphuric acid, and adding a crystal of oxalic acid, a violet colour is produced.

The production of this phenol by the action of hydrochloric or hydrobromic acid on the glycol may be explained by assuming that a chlorhydrin or bromhydrin is produced as an intermediate product, which readily loses two molecules of hydrochloric acid, just as naphthalene tetrachloride yields by dry distillation dichloronaphthalene—

$$C_{10}H_8Cl_2\left\{\begin{array}{l}Cl\\OH\end{array}\right. - 2HCl = C_{10}H_6Cl.OH.$$

Indeed, when the glycol is heated with 8—10 times its weight of hydrochloric acid in a flask connected with a reversed condenser, a body is obtained which, according to analysis, appears to be a mixture of the glycol with the chlorhydrin. Small quantities of the chloronaphthol are also produced by submitting the glycol to destructive distillation, and by heating naphthalene tetrachloride with 15 times its weight of water to 180°—190°.*

Dichloronaphthydrene glycol dissolves in fuming nitric acid without the evolution of nitrous fumes. Water precipitates the compound thus formed in white flakes, which have not yet been examined. By dissolving the glycol in 30 parts of boiling water containing 2 per cent. of nitric acid, and evaporating the solution, only phthalic acid is formed. When naphthalene tetrachloride is treated in the same way, or when it is boiled with a dilute solution of silver nitrate, a small quantity of the compound $C_{10}H_8Cl_2O_2$ is formed, besides larger quantities of the glycol and of phthalic acid.

C. S.

Coerulignone, a Product of the Wood Vinegar Manufacture.

By C. Liebermann (Deut. Chem. Ges. Ber., v, 746—749).

The crude calcium acetate, obtained by neutralising with lime the acid liquor produced by the distillation of wood, is in practice decomposed by distillation with the requisite quantity of hydrochloric acid, the crude acetic acid thus obtained being purified by the addition of potassium bichromate. Under these circumstances the crude acetic acid deposits blue films, which sink to the bottom as a violet sediment. The substance thus deposited is purified first by elutriation, and afterwards

* The author thinks that this transformation of the glycol into a phenol may explain a fact which has hitherto remained unexplained, and even been contested, namely, the transformation of benzene into phenol as effected by Church. By heating benzene dichloride with alcoholic potash he obtained phenol. This cannot be produced by the action of the potash on the monochlorobenzene formed; but it is possible that the compound $C_6H_6Cl_2$ is first converted into a chlorhydrin, $C_6H_6\left\{\begin{array}{l}Cl\\OH\end{array}\right.$, which is then resolved into hydrochloric acid and phenol.

by being dissolved in cold phenol, from which it is precipitated by means of alcohol or ether. The precipitate thus obtained consists of the new substance, called by the author *coerulignone*, in a pure state.

Coerulignone consists of small dark steel-blue needles, the composition of which is expressed by the formula $C_{15}H_{14}O_6$, or $C_{30}H_{30}O_{12}$. It is insoluble in all the ordinary solvents, and neither distils nor sublimes without change. It dissolves with a blue colour in concentrated sulphuric acid; the author, however, did not succeed in separating it from the solution in an unaltered state. It neither dyes with nor without a mordant. With acetic anhydride it yields a crystalline product, and when treated with nitric acid it is oxidised to oxalic acid. When heated with solution of potassium hydrate it gives a green liquid, which quickly becomes yellow. If the solution be concentrated till the potash begins to fuse, a point is reached at which the mass dissolves in water with an intense but fugitive violet colour. The action of hydriodic acid and phosphorus at 160° gives rise to the same colouring substance as that which is produced by the action of potash. This product, when dissolved in ether, yields an almost colourless solution, and is deposited in the amorphous state when the solution is evaporated *in vacuo*: to an alkaline solution it communicates an intense but evanescent violet coloration.

The formation of coerulignone was observed on the addition of potassium bichromate to a variety of samples of crude acetic acid, but the author is not in a position to say whether the acetic acid obtained from all kinds of wood yields this substance; he has, however, obtained it from the acid resulting from the distillation of both birch and beech wood.

Hydrocoerulignone, $C_{15}H_{16}O_6$.—This substance was obtained by the action of tin and hydrochloric acid, potassium hydrate, ammonium sulphide, sulphurous acid, or sodium amalgam on coerulignone. It crystallises well, is soluble in alcohol or acetic acid, and less so in water. It melts at 190°, and may be distilled almost without change if carefully heated, the distillate solidifying to long colourless crystals. It is also volatile to a certain extent with the vapour of acetic acid. It is converted into coerulignone by oxidising agents, and forms compounds with acetic anhydride and benzoyl chloride. Concentrated sulphuric acid dissolves it, producing an orange colour, which is changed by heating into a fuchsine red.

The above researches point to the conclusion that hydrocoerulignone exists in the crude acetic acid, and that it is converted into coerulignone by the addition of potassium bichromate. The author considers that hydrocoerulignone belongs to the series of high phenols, and that coerulignone is its quinone ($C_{16}H_{14}O_6$), or its "green hydroquinone" or quinhydrone ($C_{30}H_{30}O_{12}$). This view is confirmed by the fact that when coerulignone is allowed to remain in contact with sulphuric acid, a compound is formed which crystallises from alcohol in fine brown-red crystals, resembling those of isatin, and having the same composition as coerulignone. The author did not succeed in effecting a sharp reduction of this substance to hydrocoerulignone.

T. B.

Fisetin. By J. Koch (Deut. Chem. Ges. Ber., v, 285).

Fisetin, the colouring matter of Fiset wood, was regarded by Bolley as identical with quercetin. The author gives to it the formula $C_{15}H_{10}O_6$, which is confirmed by the analysis of an acetyl derivative, $C_{15}H_5(C_2H_3O)_5O_6$. It therefore contains one atom of oxygen less than quercetic acid, of which it is possibly the aldehyde.

On fusion with alkali, white needles, which gave the reactions of quercetic acid, were obtained, but in quantity not sufficient for analysis.

H. E. A.

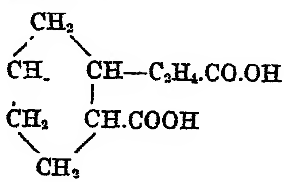
Oxybenzoic Acid. By Beilstein and Kuhlberg (Deut. Chem. Ges. Ber., v, 478).

To obtain this acid from solid chlorophenol melting at 41° (obtained from solid chloronitrophenol), it was acted upon with sodium and carbon dioxide, but only with negative results.

C. S.

Constitution of Camphoric Acid. By Felix Wreden (Deut. Chem Ges. Ber., v, 764).

When the hydrocarbon, C_8H_{14}, derived from camphoric acid, is oxidised by Thorp and Chapman's process, with a 3 to 6 per cent. solution of chromic acid liquor, about half is oxidized in a hundred hours to *isophthalic, isotolylic*, and *acetic* acids, carbon dioxide being continually evolved during the process. A small quantity of terephthalic acid also is formed, probably by the oxidation of an isomeric hydrocarbon. The author hence regards this hydrocarbon as one of the *dimethylbenzenes;* by nitration it appears to yield trinitro-isoxylene. Hence camphoric acid appears to bear to dimethylbenzene the same relation that Baeyer's hexhydrophthalic acid bears to benzene, which does not corroborate Kachler's formula—



C. R. A. W.

A New Series of Organic Acids. By P. Griess (J. pr. Chem. [2], v, 453—457).

The author has frequently mentioned a basic compound, $C_{10}H_{12}O_2N_3$, which is formed when a cold saturated alcoholic solution of amidobenzoic acid is treated with cyanogen. His endeavours to obtain this compound by the action of potassium cyanate on hydrochloride of ethyl amidobenzoate (*J. pr. Chem.* [2], iv, 293—294) led to the forma-

tion of the isomeric ethyl uramidobenzoate. He has now tried the action of ethyl cyanate on amidobenzoic acid, and finds that these two substances unite and yield a body having the composition $C_{10}H_{12}N_2O_3$, but not identical either with the first-mentioned basic compound or with ethyl uramidobenzoate—

$$C_7H_7NO_2 + C_3H_5NO = C_{10}H_{12}N_2O_3.$$

The new compound is a well-marked acid, changing vegetable colours, and completely neutralising the strongest bases. It is soluble with difficulty in water, and crystallises from water or from weak spirit in fine white shining needles. It is easily soluble in hot alcohol, but not very soluble in cold alcohol or ether. The spontaneous evaporation of its alcoholic solution gives rise to six-sided tables or small prisms. When heated it melts to a yellow oil, and at a higher temperature froths and evolves irritating vapours. It is not altered by hydrochloric acid, but is decomposed by a strong boiling solution of potash, ammoniacal vapours being evolved. Nitric acid converts it into a nitro-compound crystallising in yellow needles. The *barium salt*, $(C_{10}H_{11}N_2O_3)_2Ba$, forms microscopic needles, easily soluble in cold water; when air-dried it retains 3 molecules of water. The *silver salt*, $(C_{10}H_{11}N_2O_3)Ag$, forms small white shining needles.

The author regards this acid as ethyl-uramidobenzoic acid—

$$C_6H_4\left(\left.\begin{matrix}CO\\C_2H_5\\H_2\end{matrix}\right\}N_2\right)'(CO_2H)'.$$

Analogous acids were obtained by the action of ethyl cyanate on amidodracylic acid and on anthranilic acid.

Since making these researches the author has seen the paper of Cahours and Gal (*Compt. rend.*, lxxi, 462), and concludes from it that these investigators have already obtained the same acid as that described in the present paper.

T. B.

Action of Bromobenzene on Aniline. By MERZ and WEITH (Deut. Chem. Ges. Ber., v, 646).

POTASSIUM is readily dissolved by aniline. On heating the product with bromobenzene a comparatively small quantity of *diphenylamine* and a larger of *triphenylamine*, $N(C_6H_5)_3$, are obtained. This compound is sparingly soluble in alcohol, more readily in petroleum-naphtha, and crystallises in large thick plates, melting at 126°—127°, and boiling at a high temperature. With different reagents it gives blue or green colours. Triphenylamine may also be obtained by the same reaction from diphenylamine.

Sodium does not act on aniline, and may be kept under bromine, which acts violently on potassium.

C. S.

Diphenylamine. By MERZ and WEITH (Deut. Chem. Ges. Ber., v, 283).

THE authors have commenced the study of the chemical behaviour of diphenylamine, the imidogen base *par excellence* of the aromatic series.

The commercial product is, with the exception of traces of aniline, pure; it crystallises from ligroin in large plates, like naphthalene, and melts at 54°.

It is slowly acted upon by concentrated sulphuric acid at 150°—160°, and converted into a mixture of *diphenylamine-monosulphonic* and *disulphonic acid*, which may be separated by fractional crystallisation of the barium salts, since the salt of the mono-acid is difficultly soluble, whilst that of the disulpho-acid is easily soluble in water. The action of oxidising agents on the solution of these sulpho-acids, or their salts, gives rise to a variety of characteristic colorations.

Acetyldiphenylamine, $N(C_6H_5)_2C_2H_3O$, is obtained by the action of acetyl chloride on diphenylamine.

Carbon disulphide has no action on diphenylamine.

Chlorocarbonic ether and diphenylamine give the compound, $N(C_6H_5)_2.COOC_2H_5$. H. E. A.

Cystine. By J. DEWAR (Pharm. J. Trans. [3], iii, 144).

BY the action of nitrous acid, cystine yields a product corresponding in its characters with the syrupy modification of pyruvic acid. Cystine being therefore probably $C_3H_5NO_2S$, its constitutional formula may be written in five ways:—

Pyruvic acid.	I.	II.	III.	IV.*	V.
CH_3	CH_2NH_2	CH_2NH_2	$CH_2(NH_2)$	$CH\begin{cases}NH_2\\SH\end{cases}$	CHS
CO	CO	CO	CS	CO	$C\begin{cases}NH_2\\H\end{cases}$
$CO{\cdot}OH$	$CO.SH$	$CSOH$	$CO.OH$	$CO.OH$	$CO.OH$

From a body of the constitution of No. 5, if we replace the sulphur by hydrogen, we ought to obtain alanine; from No. 3, β-alanine; from 4, amidolactic acid (serine); from 2, amidoglycerin; while in No. 1 the sulphur is hardly replaceable in this way. In an experiment with cystine and sodium amalgam, no alanine could be obtained.

When cystine was heated with baryta water for some hours to 130°, a yellow syrupy acid was produced, mixed with a few crystals resembling Finck's uvitic acid. The ammonia salt gave a white amorphous precipitate with argentic or mercurous nitrate, a red colour with salts of iron, and no precipitate with cupric sulphate. The barium salt was non-crystalline, the acid lost the power of colouring ferric salts after treatment with sodium amalgam, and the silver-salt corresponded to pyruvic acid.

Normal *thio-pyruvic acid*, obtained from dichloropropionic ether by treatment with excess of alcoholic potassium sulphide, is deposited from ether in yellow crystalline plates, also as a viscid liquid. The lead

* The formula IV does not agree with the rest, as it contains 3 atoms of oxygen. —ED.

and silver-salts are white, insoluble, and blacken when heated; the mercurous compound is black from the first. The calcium, barium, iron, cadmium, and copper-salts are all soluble. The potassium and sodium salts are yellow, slightly decomposed by air, and in contact with tin and sulphuric acid, evolve hydrogen sulphide.

Thiocarboxyl-pyruvic acid has not yet been obtained in a pure state. Pyruvic acid reacts violently on phosphorus pentasulphide, but the product on distillation is very small. Chloropyruvyl treated with potassium sulphide will probably furnish a better yield. The author intends to transform these acids into amido-compounds, with the view of obtaining artificial cystine.

C. G. S.

Methylguanidine. By N. TAWILDAROW (Deut. Chem. Ges. Ber., v, 477).

THIS compound having the constitution $C\begin{cases}NHCH_3\\ NH\\ NH_2\end{cases}$, is produced by the action of methylcyanamide on ammonium chloride; it forms a double platinum chloride, crystallising in oblique rhombic crystals.

C. S.

Synthesis of Parabanic Acid. By BASAROW (Deut. Chem. Ges. Ber., v, 477).

BY heating oxamide with phosgene to 170°—180°, and exhausting the product with water, a compound is obtained, possessing all the properties of parabanic acid. C. S.

Comparative Examination of Purpurates and Isopurpurates. By E. KOPP (Deut. Chem. Ges. Ber., v, 644).

THE best yield of potassium isopurpurate is obtained by mixing intimately finely powdered picric acid with twice its weight of potassium cyanide and a little water. After half an hour more water is added, and the mixture heated to 40°—45°, and then allowed to cool; the crystals separating out are pressed and purified according to Hlasiwetz's method.

In dyeing with isopurpurates the same mordants are used as in dyeing with murexide, the best mordants being mercury- and lead-salts. Murexide produces on mercury mordant a splendid purple with a violet tint, while isopurpurates dye purple having a brownish orange tint; the colours produced by the latter are neither acted upon by sunlight nor by sulphurous acid, which quickly destroys murexide. On silk mordanted with zinc, murexide gives a fine yellow, and isopurpurates a dark, reddish-brown. Murexide colours are destroyed by acids and alkalis, whilst those of the isopurpurates assume only a yellowish tint. Purpurates are not explosive; by adding hydrochloric acid to a somewhat concentrated solution, it becomes colourless, and after some time dialuramide crystallises out. Nitric acid oxidises them to alloxan, and

when caustic soda-solution is added to a solution of a purpurate, the solution becomes first bluish-violet, and on standing, or more quickly on heating, colourless.

Isopurpurates explode on heating, some very violently; on adding hydrochloric acid to a solution, it becomes yellowish-brown and opaque, and afterwards brown amorphous flakes separate out. Nitric acid changes their colour into orange, and caustic soda in the cold to brownish violet, whilst on heating ammonia is given off, and the colour is changed into a dark yellowish-brown. Isopurpurates are also decomposed by ammonia, but more slowly than by the fixed alkalis. Hydrogen sulphide reduces ammonium isopurpurate, sulphur separating out, while the liquid becomes yellowish-red, and assumes a dirty colour when exposed to the air. The products of decomposition of isopurpuric acid are still colouring matters, dyeing silk like the aniline-browns (Vesuvian or Bismark).

C. S.

Action of Mustard-Oil on Milk. By Dr. SCHWALBE (Deut. Chem. Ges. Ber., v, 286).

THE author finds that the addition of mustard-oil to cows' milk (1 drop to 20 grms.) prevents coagulation. The mixture may be kept in summer for weeks in half-filled bottles, without coagulation taking place; after 5—7 weeks the casein was found to be converted into albumin, and the liquid was strongly acid. The change appears to consist in an oxidation of the casein.

H. E. A.

On Koumiss. By H. SUTER-NAEF (Deut. Chem. Ges. Ber., v, 286).

THE author has examined the koumiss manufactured in Davos, in imitation of the true Russian koumiss. At 50° it has a mean specific gravity of 1·1286.

It contains	In 100 grms.	Per litre.
Water	90·346	80·62
Alcohol............	3·210	36·22
Lactic acid	·190	2·56
Sugar	2·105	23·76
Albuminates	1·860	20·99
Butter	1·780	20·08
Inorganic salts......	·509	5·74
Free carbonic acid ..	·177	1·99

It contains more sugar and less lactic acid than old Russian koumiss, and is probably prepared by adding a few per cent. of sugar to skim-milk, alcoholic fermentation being induced by the addition of yeast.

H. E. A.

Physiological Chemistry.

On the Nutrition of Muscular and Pulmonary Tissue. Part 1st. On the Nutrition of Muscular Tissue in Health. By W. Marcet (Phil. Mag. [4], xliv, 349—365).

The author considers that tissues are formed of (1.) The nutritive material which has left the blood and is on its way to become assimilated (2.) The fully developed or ripe tissue. (3.) The material resulting from the waste of tissues, which is on its way out as effete matter.

The first of these constituents in muscle is the colloïd material, soluble in water; the second. the fibrous mass, insoluble in water; the third, the crystalloïd matters, soluble in water. These were separated by extracting muscle with water, when the first and third were dissolved out and the second remained behind. The watery extract was then boiled so as to coagulate the albuminous substances in it. The crystalloïds were separated by filtering, washing the coagulum and evaporating, and these the author takes to represent the third constituent.*

Phosphoric acid and potash are present in the watery extract of muscle in a colloïd condition (possibly because combined with albumin. Compare Pribram, *Ludwig's Arbeiten*, vi, p. 67).

The colloïd substances, albumin, phosphoric acid, and potash, contained in the total watery extract bore very nearly the same relation to each other as those contained in the insoluble or mature muscle. The author therefore thinks that the material destined to become transformed into the insoluble portion of flesh or ripe tissue undergoes a mere morphological change, one molecule of the ripe tissue as it wastes being replaced by one molecule of the nutritive material having the same composition. The crystalloïd constituents of the watery extract contained an amount of nitrogen which corresponded only to about ⅔rds of the soluble or nutritive albumin in the extract, whence follows that ⅓rd of the whole nutritive material present in flesh is in store and not for immediate use. Phosphoric acid and potash are present in the effete material exactly in the right proportion to form potassium pyrophosphate.

Soda and potash are present in very small proportion in the watery extract, and entirely absent from the insoluble part of muscle.

In the flesh of salmon the proportion of nutritive albumin is twice as large as in ox-flesh, and about ⅔rds of the amount of this substance is in excess of that required for immediate use. The necessity for this large store may be accounted for by a consideration of the rapid growth of the fish.

T. L. B.

* It appears to the abstractor that this method is not quite satisfactory, as the peptone-like bodies contained in muscle (Kühne, *Lehrbuch d. Physiolog. Chemie* p. 289) are thus included among the effete products, while there is no proof that they are not present for the purpose of nutrition.

The Bile-Pigments and their Detection by the Spectroscope. By B. I. Stokvis (Deut. Chem. Ges. Ber., v, 583—585)

When icteric urine is treated with a small quantity of zinc chloride, and afterwards with ammonia in excess, the fluid becomes brownish-green when filtered or shaken with air. In the spectroscope it gives three characteristic absorption-bands and a disappearance of the rest of the spectrum, commencing in the blue between the lines *b* and F'. The first band, dark and sharply defined, lies in the red between C and D, the second less distinct between D and E, and the third, small and indistinct, between D and E, in the green and nearer E. The latter band is also seen in urine to which no zinc chloride and ammonia have been added, while the two former occur only in uteric urine This spectroscopic reaction will serve as a test for bile-pigment in the urine. In order to obtain it in sufficient quantity, Stokvis recommends that from 200 to 300 c.c. of the urine should be precipitated by neutral lead acetate and the precipitate treated with alcohol containing oxalic acid. The brownish-yellow fluid which results gives the absorption bands after a little time, when treated with ammonia and zinc chloride.

Stokvis has endeavoured to prepare the substance which gives this spectrum from bilirubin and biliverdin. From both these it can be formed by the action of ammonia and zinc chloride.

From bilirubin it can also be prepared by various other methods, which are given. The simplest plan is to add to an alcoholic solution a few drops of tincture of iodine, to boil it, and then shake it vigorously with air.

The substance is an oxidation-product and not a zinc-compound of bile-pigment. It is more highly oxidised than bilirubin and biliverdin, and also more highly oxidised than bilifuscin and biliprasin, as it can be formed from these latter in the same way. Stokvis calls it choleverdin. The mode of formation and the properties of choleverdin indicate that it stands in close relation to Gmelin's oxidation-products.

Among the properties of this substance are, that its neutral solutions fluoresce into red, while of its alkaline solutions only the ammoniacal fluoresce, and that it is soluble in alcohol, ether, chloroform, and amylic alcohol; but in the case of the latter three, not out of alkaline solutions.

A reducible product of choleverdin is also described. It exists in a great number of fluids which contain bile-pigment or its products. Even when the oxidation has gone so far as that no reagent is able to indicate the presence of bile-pigment, the reducible substance may be detected. It is best obtained from gall-stones. The method of preparation is given in the original. Its properties, so far as they have been investigated, are, that it is easily soluble in water and alcohol, less so in ether and chloroform, very stable in acid solutions, but not at all so in alkaline ones. After reduction the solution is red, but contains no bilirubin.

D. F.

Is Pure Carbolic Acid (Phenol) Non-Poisonous?
By T. HUSEMANN (Chem. Centr., 1872, 488).

HAMBERG has expressed the opinion that pure carbolic acid is not poisonous, and that the poisonous action which has been observed is to be referred to the presence of impurity. Husemann, however, states that pure phenol of commerce, even after repurification by solution in a limited quantity of water, according to Church's process, is undoubtedly poisonous when administered in solution, either by the mouth or by subcutaneous injection.

W. A. T.

Action of Brucine, Emetine, and Physostigmine on the Organism.
By PANDER (Chem. Centr, 1872, 437).

BRUCINE acts chiefly on the liver; it is partly discharged from the system by the kidneys. Fermentation does not affect brucine.

Emetine acts chiefly on the stomach, liver, and blood; it is partly discharged by the kidneys. When exposed to a fermentative action it suffers decomposition.

Physostigmine is partly discharged in the spittle, part of it finds its way into the blood and bile; it is also found in the stomach and liver. Fermentation decomposes this alkaloid.

M. M. P. M.

Chemistry of Vegetable Physiology and Agriculture.

On the Chemical Processes in the Plant.
By A. EMMERLING (Deut. Chem. Ges. Ber., v., 780—785).

WITH the object of extending the very slight knowledge that we possess of the chemical processes which occur in the plant, the author has set himself the task of ascertaining the action of the plant-acids (oxalic, tartaric, malic, etc.) on those mineral salts which are of importance in the nourishment of plants. To this end he has examined, in the first instance, the behaviour of oxalic acid towards the nitrates of calcium, potassium, and sodium; having chosen this case, because there is no doubt that plants in general take up nitrates from the soil, and because it is equally certain that oxalic acid is present in most plants.

The action between solutions of oxalic acid and calcium nitrate was determined under all possible conditions, regard being paid to the influence of time, of concentration, of an excess of the one or the other reagent, and of the presence of other salts. The reaction consists in the separation of crystalline calcium oxalate and of free nitric acid. The amount of oxalate precipitated depends on the conditions of experiment; it is less the greater the dilution and the shorter the time of action. Even when highly dilute solutions are employed, however, the

amount of precipitate is very considerable, and if the action be continued sufficiently long, almost complete precipitation is effected, the formation of a precipitate ceasing to take place only when the solutions are enormously diluted. The separation of oxalate is not only increased by an excess of calcium nitrate, but also by an excess of oxalic acid; nitric acid has a contrary action. From these results the author concludes that the plant-juices *necessarily contain free nitric acid.* With regard to the crystalline form which the deposited calcium oxalate takes, he finds that it is exactly that which is of most common occurrence in plants; the crystals separate in monoclinic prisms of the orthoclase form, possessing an extraordinary tendency to form twins, and frequently united in aggregates such as are often met with in plants, and known as "morning stars." Raphides were not observed.

By applying the method of diffusion the author has also succeeded in establishing the fact, that the nitrates of the alkalis are partially decomposed by oxalic acid in very dilute solution, with separation of free nitric acid.

Although, in the author's estimation, there is no doubt of the separation of nitric acid in the plant, he does not believe that it long remains present as such, but that it is probably further converted by reduction into ammonia or hydroxylamine, which in turn takes part in the formation of organic nitrogen-compounds.

H. E. A.

Alcoholic Fermentation. By J. B. DUMAS (Compt. rend., lxxv, 277—295).

THE author holds that fermentation is the chemical decomposition of sugar by the vital force of yeast-cells, and considers that Pasteur's researches have placed the matter beyond dispute. He has himself made a number of experiments, the results of which are opposed to the views of Berzelius and of Liebig, and show that fermentation is not merely set going by the ferment, but is continuously dependent upon it, and susceptible of measurement and modification like any other chemical phenomenon.

In one series of experiments he endeavoured to transmit the movements of a fermenting solution of sugar to a solution of pure sugar separated from it either by various liquids or by a septum of collodion, or else resting upon it in direct contact, and failed in every case to do so, or even to cause the inversion of the sugar.

Berzelius having attributed the fermentation of sugar to the contact-action of the yeast, the author tried the effect upon sugar of another chemical phenomenon also attributed to contact, namely, the liberation of oxygen from hydrogen dioxide and manganese dioxide. This was effected in a solution of sugar, and produced no change whatever in it. Various other chemical actions excited in a solution of sugar are stated by the author to have been also without any effect upon it; so that its alcoholic decomposition cannot apparently be produced by another chemical action.

Schönbein has shown that ozone and hydrogen dioxide are formed during slow combustions, and among these Liebig classes fermenta-

tions; but the author has not found that either ozone or hydrogen dioxide is produced during fermentation. Oxygen passed through a fermenting liquid does not appear to affect it in any way.

By dividing a mixture of yeast and water equally among solutions of sugar, the yeast being always in excess, it was found that under similar circumstances as regards pressure and temperature, the duration of the fermentation was proportional to the quantity of sugar. Cane-sugar requires twice as long for its fermentation as glucose; so that as much time is required to invert the sugar as to ferment it. The author estimates that about 400 milliards of yeast-cells are required to ferment a solution of one gram of pure cane-sugar in one hour. Fermentation proceeds more slowly in darkness, and in a vacuum.

Neutral gases do not affect the power of yeast. *Sulphur*, in a fermenting liquid, is converted into hydrogen sulphide having an odour of onions, and appears to be the only substance, besides sulphuretted compounds, that enters into reaction with ferments. Yeast is by this reaction shown to be a reducing agent. Sulphur does not appear to hinder fermentation, as it has been stated to do. Very dilute *acids* do not affect fermentation: larger doses destroy it. Very dilute *alkalis* retard fermentation: larger doses arrest it. *Alkali carbonates* hinder it only in very large doses.

Sal-ammoniac causes yeast to precipitate almost as rapidly as potato-starch deposits from water. *Potassium silicate* and *borax* coagulate it, so that it becomes clotted like silver chloride.

When fresh yeast is placed in a saturated solution of *neutral potassium tartrate*, no change is perceived, and on removing the yeast to a solution of sugar, fermentation almost instantly commences, and rapidly follows its course. But the liquid, after the fermentation, presents all the characters of a solution of ordinary albumin. When the tartrate, the yeast, and the sugar and water are mixed together at once, no such effect is produced; so that it must be caused in the other case by, 1st, the absorption of the saline solution by the yeast, and 2ndly, the displacement of this by the sugar solution. The action of the neutral tartrate and of such salts as potassium silicate, borax, soap, etc., can, therefore, effect a physiological analysis of yeast, similar to that of blood by the action of certain neutral salts.

The *acid tartrate of potassium* and some other salts seem rather to favour fermentation; others retard it; others, again, permit inversion of the sugar to occur, but prevent its fermentation, such as *common salt*, while others altogether prevent both inversion and fermentation, those being *potassium cyanide*, *potassium monosulphide*, and, strange to say, *potassium acetate*.

Sodium sulphites and *thiosulphate*, and *potassium sulphocyanate* furnish, by a fermentation which sometimes soon ceases, and sometimes continues to its natural termination, an alcoholic liquid which, when distilled with solution of potash, yields an alcohol containing aldehyde and a matter exhaling a very agreeable fruity odour. The alcohol becomes milky when mixed with water. The solution of potash deposits much aldehyde-resin on cooling, and yields on evaporation salts having special characters.

Potassium thiosulphate disengages hydrogen sulphide during the whole of the fermentation, and the product which accompanies the alcohol exhales an odour of garlic.

Lastly, with regard to the action of salts as bearing upon the theory of fermentation, it may be mentioned that when, as in the presence of the acid potassium tartrate, fermentation proceeds actively, the yeast-cells are clear, well-defined, and full of a plastic matter containing brilliant and very active corpuscles, and send out numerous offshoots; whereas, when the fermentation languishes, as in the presence of salts of iron or manganese, the cells appear contracted, tuberculated, granular, and shrivelled, and without recent offshoots.

E. D.

Ferments belonging to the Diastase Group. By J. B. DUMAS (Compt. rend., lxxv, 295).

A SOLUTION of borax coagulates yeast, and the supernatant liquid cannot, like yeast-water, invert cane-sugar. The author finds that borax prevents the action of yeast-water upon sugar; that it prevents the action of synaptase upon amygdalin, the action of diastase upon starch, and the action of myrosine.

E. D.

New Experiments Demonstrating that Wine-producing Yeast-germs are not formed within the Grape. By L. PASTEUR (Compt. rend., lxxv, 781).

SOME must of grapes was boiled in a number of flasks, each provided with an open sinuous neck, and a second one drawn out to a fine point and sealed. The point of the sealed neck of each flask was thrust into a grape and broken off within it. After drawing a drop of the fresh juice into the flask, the drawn-out neck was at once sealed again. Out of ten quantities of must thus treated, only one underwent fermentation. In these experiments the boiled must in the flasks was found to ferment very soon after adding some of the washings of a piece of grape, which contained a multitude of organic corpuscles.

E. D.

Generation of Ferments. By E FRÉMY. Reply by L PASTEUR (Compt. rend, lxxv, 782—784).

PASTEUR has only examined fermentation set up by fungi, and his researches afford no explanation of the direct fermentation of the must caused by the ferment which, Frémy asserts, is produced by the cells of the grape itself.

The correctness of Frémy's assertion is denied by Pasteur. Neither the albuminoid matters of the grape, nor the cells of its parenchyma, are capable of being transformed into yeast-cells.

E. D.

New Facts for the Theory of True Fermentations. By L. PASTEUR. **Observations thereon.** By E. FRÉMY (Compt. rend., lxxv, 784—791).

IF a saccharine liquid suitable for fermentation be put in a vessel in which it can be sown with a particular organism, without fear of any other getting into it spontaneously from the air, unknown to the operator, and then a trace of pure *Mycoderma vini* be sown in it, it will become covered all over with a pellicle of the fungus in a few days. This can be shown to grow at the expense of the air, absorbing its oxygen, and giving out nearly the same volume of carbon dioxide, and to produce no alcohol in the liquid. If now the pellicle be submerged in the liquid, bubbles of carbon dioxide soon begin to rise from it, and alcohol is formed; at the same time its cells swell up and cease to multiply, and the internal structure of their plasma becomes very greatly modified. Thus, in this experiment the same cells acquire or lose the power of acting as a ferment, according as they are deprived of air, or exposed to its action. This experiment also succeeds with the true fungi, such as *Penicilium glaucum.*

Yeast and other ferments therefore differ from the other lower organisms only in possessing the faculty of living and multiplying regularly and continuously without contact with the atmosphere. These observations appear to remove the mystery of fermentation. Instead of requiring free oxygen to burn the materials which serve for their nutrition, they obtain the heat necessary to their existence by living upon oxygenated bodies like sugar, which can furnish heat by their decomposition.

Viewing fermentation in this light, all living bodies may become ferments under certain conditions. Thus, when an animal is suddenly killed, life does not at once cease in the organs of the body, or in the physiological elements of these organs, and when this goes on in them without the influence of free oxygen, it does so at the expense of the surrounding materials from which the necessary heat is obtained, and they behave like ferments to these materials.

Bérard has shown that when fruits are exposed to the air they absorb oxygen and replace it by carbon dioxide, but that when placed in an inert gas, like carbon dioxide itself, they also evolve carbon dioxide. The gas evolved under the latter circumstances he considers to be a product of a sort of fermentation. Pasteur confirms this view, for he finds that alcohol is then also formed, that is, when the fruit is placed in an inert gas. Pasteur has assured himself, too, that when this experiment is made with suitable precautions, no beer-yeast or other ferment is produced.

Grapes thus exposed to carbon dioxide acquire at the same time exactly the odour and flavour of expressed grape-juice, quite distinct from that of the fresh grape.

E. Frémy, seizing on the statements made by Pasteur respecting fermentation in fruits, asks whether it is not evident, if a fruit ferments in carbon dioxide, and consequently under conditions in which it can receive nothing from the air, that ferments are produced directly

by the influence of the organisation within the cells themselves, and that their generation is not due to germs which may exist in the air.

Pasteur's reply is that he has ascertained that neither yeast-cells nor any organised ferment whatever are developed in the interior of the fruits.

E. D.

Confirmation of some of the Chemical Phenomena described by M. Pasteur. By A. TRECUL (Compt. rend., lxxv, 791—793).

WHEN pieces of the leaf of *Aloe socotrina* are macerated in water, the liquid becomes red by the action of the air on the aloin dissolved in it, but as minute infusoria become developed in it, and its surface gets covered with fungi, which exclude the air, the liquid acquires a yellow colour by the reproduction of aloin.

The *amylobacteria* which the author wished to study in making this experiment may be observed living in perfectly closed cells, even in thick-walled liber-cells. Their generation can take place in closed cells, the plasma of which contains no granular matter. They are examples of bodies which live under conditions analogous to those under which yeast vegetates, and are certainly not generated by germs derived from the atmosphere. Is Pasteur quite sure that nothing analogous is developed in the interior of fruits in which, when placed in carbon dioxide, fermentation takes place?

E. D.

Antifermentescible Substances. By A. PETIT (Compt. rend., lxxv, 881—883).

THIS is a note upon substances preventing fermentation—antiferments, therefore, rather than antifermentescible substances.

When the solution of cane-sugar contains 1 per cent. of sodium silicate, fermentation commences slowly after the addition of the yeast, but when established it proceeds rapidly and very regularly. 1 per cent. of borax has no effect on fermentation. The same proportion of ferrous sulphate causes the fermentation to proceed slowly but regularly. With copper sulphate the fermentation commences, but soon stops. With 1 per cent. of arsenic trioxide the fermentation proceeds slowly, but very regularly.

Acetic acid the author finds to be more antifermentescible than the same quantity of a mineral acid. 1 per cent. of oxalic acid markedly slackens the rate of fermentation.

The author has completely fermented a 25 per cent. solution of alcohol, a 5 per cent. solution of glycerin, and a 1 per cent. solution of succinic acid.

The most antifermentescible bodies tried are mercuric oxide and chloride.

Sulphites do not hinder fermentation, and are themselves converted into sulphates as the fermentation proceeds.

E. D.

On the Antiseptic Properties and Physiological Action of Sodium Silicate. By A. RABUTEAU and F. PAPILLON (Compt. rend., lxxv, 755).

ONE per cent. of sodium silicate prevents the alcoholic fermentation in grape-juice. Urine containing 2 per cent. of the salt undergoes no decomposition, even in 15 days, and the evolution of ammonia is scarcely sensible with 1 per cent. Milk mixed with one-fourth of its volume of water containing one twenty-fifth part of the silicate, remains free from acidity at the end of five days, and if the cream be then removed, the remaining liquid will be found to be alkaline, and without a single flake of casein. An emulsion of three sweet and three bitter almonds made with water containing one twenty-fifth part of the salt is quite inodorous, and remains so at the expiration of ten days. It appears then that silicate of soda, like borax, prevents fermentation and putrefaction, only its action is more energetic. 2 grams of borax dissolved in 40 grams of water, and injected into the veins of a dog, produced no appreciable effect upon the health of the animal; while an injection of 1 gram only of sodium silicate under the same conditions caused death. In the latter case the effects produced were purging and vomiting, and the urine contained albumin; the appetite gradually diminished, and the animal died in nine days. J. B.

Vegetable Parasites of Bread. B. F. ROUCHARD and C. LEGROS (Compt. rend., lxxv, 758).

THE mouldiness which is sometimes developed in bread does not result from the presence of certain germs in the atmosphere, but occurs when the bread is badly made from inferior flour and kept under wrong conditions. Of the orange-coloured cryptogams observed, the *Oidium aurantiacum* was not nearly so abundant as the *Thamnidium*, the latter being one form of development of *Mucor Mucedo*. The green spots are produced, sometimes by *Aspergillus glaucus*, and sometimes by *Penicilium glaucum;* the black spots by *Rhisopus nigricans;* the white spots by *Mucor Mucedo*, and sometimes there is also *Botrytis grisea*. Excess of salt added to the bread prevents the production of these fungi. J. B.

Composition of "Candle Nuts," and of the Nuts and Oil-cake of the Cocoa-palm. By G. NALLINO (Gazzetta Chimica Italiana, ii, 257—262).

I. *Candle-nuts*, so called from their property of easily taking fire and burning with a bright flame like ordinary candles, are the seeds of *Aleurites triloba*, Forst (*A. Ambinux*, Pers; *A. moluccana*, Wild; *Croton moluccanum*,* Linn.), a shrub belonging to the order *Eufoibraceæ*, tribe, *Acalifæ*, indigenous in the Moluccas and in some of the islands of the Pacific. They are also known by the name of *Bancoul nuts*, and in Taiti by that of *Taïli*.

*According to Müller. By Jussieu, on the other hand, it is referred to the tribe *Crotoneæ*, and by Baillon, to *Jatrafideæ*.

The fruit of *Aleurites triloba* is formed of two large fleshy drupes adhering laterally, and divided internally into two cells, each of which contains a single indehiscent seed of the size of a common nut, and covered, especially in the furrows, with a thin whitish skin of earthy aspect, beneath which is the shell, of blackish colour, and very hard. The kernel is white, and formed of a large oleaginous albumen, surrounding the homotropous embryo, which is provided with thin membranous cotyledons rather narrower than the albumen

The seeds are usually sent to Europe deprived of their shells, which are used as fuel. The imperfect combustion of these shells serves in Taïti for the preparation of a kind of lampblack, used by the natives in tattooing. In the same locality the bark of the shrub is used for the manufacture of various textile fabrics.

The fresh kernels have a not unpleasant taste, but are difficult to digest, and exert a purgative action, even in moderate doses. In the islands of the Pacific they are eaten only after slight torrefaction, which renders them innocuous. They are, however, chiefly used by the natives for the extraction of oil for burning. The shelled kernels quickly turn rancid, acquiring a yellow-brown colour and a disagreeable taste. The fat extracted from them is subject to similar alterations. This fat is used in Europe solely for soap-making. The oil-cake forms an excellent manure.

The average weight of the shells is 6·5 grams; of the kernels, 3·3 grams.

Composition of the Shells.

Water	3·71
Organic matter	89·90
Mineral matter	6·39
	100·00

Composition of the recently shelled Kernels.

Water	5·25
Fat (extracted by carbon bisulphide)	62·97
Cellulose and other organic matters	28·99
Mineral matter	2·79
	100·00

Nitrogen, 3·64 p.c.

Composition of the Ash of the Kernel.

	In 100 parts of ash.	In 100 parts of the almonds in their natural state.
Lime	18·69	0 52
Magnesia	6·01	0·17
Potash	11·33	0·31
Phosphoric anhydride	29·30	0·82

The fatty matter extracted from the kernels by carbon bisulphide at ordinary temperatures forms a transparent, amber-yellow, syrupy liquid. When cooled to $-10°$ it becomes viscous, but neither loses its transparency nor changes colour.

II. *Cocoa-nuts.*—The fatty matter extracted from these nuts is used

almost exclusively for the manufacture of toilet soap. The cake left after the extraction of the fat is used in England as fodder for cattle, in Italy as manure.

The oil-cake of the cocoa-nut was examined some years ago by Grouven (*Wochenblatt der Annalen der Landwirthschaft*, 1866, p. 453), who found:—

In 100 parts of the air-dried oil-cake—

Proteids.	Oil.	Cellulose.	Water.
21·20	8·60	7·70	9·36;

and in 100 parts of the ash (CO_2 deducted)—

K_2O.	Na_2O.	CaO.	MgO	Fe_2O_3.	P_2O_5.	SO_3.	SiO_2.	Cl.
40·57	2·30	4·71	2·95	3·54	26·98	3·78	3·38	13·42

As, however, the cocoa-nuts now sent to Europe are of selected quality, and more carefully freed from the other parts of the fruit than formerly, and as, moreover, many improvements have been made in the extraction of the fat, the author of this paper has thought it worth while to make a fresh examination of the cocoa-nut and of the oil-cake, such as is obtained for the soap-works of Cav. Mazzuchetti, in Turin, and sent in large quantities to England as fodder for cattle.

	Cocoa-nuts in the natural state.	*Oil-cake from Mazzuchetti's Soap-works.*
Water....................	5·80	11·89
Fat (extracted by CS_2)	67·85	12·34
Cellulose „	24·80	69·66
Mineral substances	1·55	6·11
	100·00	100·00

100 parts of the fresh oil-cake contain 2·75 per cent. nitrogen, and 100 parts of the ash contain 24·35 per cent. phosphoric anhydride.

H. W.

On the Assimilation of Phosphates by Barley. By A. Perepelkin (Deut. Chem. Ges. Ber., v, 478).

In contradiction to Lewitzky (*Deut. Chem. Ges. Ber.*, iv, 935) the author finds that soluble phosphates are more readily absorbed by plants than insoluble ones. By growing Himalaya barley in artificial soil, the largest yield of grain was obtained by employing potassium phosphate, a lesser yield by using calcium phosphate, whilst iron phosphate gave the worst result.

C. S.

Christiani's Field Experiments at Oderbruch. By A. Stöckhardt (Chemischer Ackersmann, 1872, 103—104, and 148—168).

The Oderbruch morass was drained in 1753. The present soil is rich in clay and humus, and of great fertility. From 1827 to the present

time three plots have been the subject of experiment, one unmanured, one receiving about 17 tons, and one 25½ tons of dung per acre. Up to 1859, the manure was applied once in four years, since then once in three years. During the first 25 years the crops were chiefly corn, the other crops being six of potatoes and two of winter rape. Up to this point the produce of the unmanured soil was almost as great as that of the manured. In the 18 years, 1852–69, mangolds were chiefly grown, the other crops being five of barley. With this mode of cropping exhaustion became very evident. The average produce of the crops was as under. The grain and potatoes are given in bushels, and the roots in cwts. per acre.

Crops.	Unmanured.	Dunged.	Strongly dunged.
Oats, 5 crops, 1829—51	76·9	82·6	86·4
Barley, 8 crops, 1828—50	51·5	61·7	61·7
Wheat, 4 crops, 1837—48	38·3	40·7	42·6
Potatoes, 6 crops, 1827—49	233·3	273·8	283·3
Mangolds, 12 crops, 1852—68	147·3	278·7	315·7
Barley, 5 crops, 1855—69	35·9	51·4	47·6

After 1859 half of the unmanured plot was liberally dressed with dung; the produce on this half at once rose to that of the continuously manured plots.

In 1856, and again in 1869, samples of the unmanured and heavily manured soils were analysed by different chemists. Unfortunately the analyses represent the unmanured soil as richer in 1869 than it was in 1856! The percentage results in 1869 were as follows:—

	N.	N. as $NH_3 + N_2O_5$.	K_2O.	CaO.	MgO.	P_2O_5.	SO_3.	SiO_2.
Strongly dunged..	·340	·0182	·214	·614	·617	·262	·036	·252
Unmanured	·288	·0128	·208	·481	·167	·233	·031	·275

In the barley crop of 1869 the nitrogen and potash were determined. The grain from the different plots varied little in composition, but the straw from the unmanured plot was found poorer in both ingredients.

R. W.

Analytical Chemistry.

New Process for Estimating Free Oxygen. By SCHÜTZENBERGER and GÉRARDIN (Compt. rend., lxxv, 879—881).

ACCORDING to the authors, sodium hyposulphite* absorbs oxygen so

* Hyposulphurous acid, SH_2O_2, the sulphur analogue of formic acid—called *hydrosulphurous acid* by Schutzenberger, who discovered it (*Zeitschr. f. Chem.*, 1869, 545)—is produced by *deoxidation* of sulphurous acid. The acid $H_2S_2O_3$, produced by *sulphuration* of sulphurous acid, and commonly known as hyposulphurous acid, is better called *thiosulphuric acid*, as proposed some years ago by Dr. Odling.—ED.

rapidly that it may be advantageously employed in estimating the amount of oxygen in a gaseous mixture, or of oxygen dissolved in a water. The reaction consists in the conversion of the hyposulphite into the acid sulphite of sodium, and the authors determine the amount of hyposulphite thus oxidised by a water by means of Coupier's soluble aniline-blue, which is instantly decolorised by the hyposulphite and not affected by the acid sulphite. Sodium hyposulphite also decolorises an ammoniacal solution of cupric oxide, while the sodium sulphites do not, and the authors use this solution as a means of titrating the test-solution of hyposulphite. It is necessary to exclude the air from the water during its treatment with the hyposulphite, and for this purpose it is covered with a thin layer of oil, beneath which the beak of the burette is made to dip. The hyposulphite solution is prepared by putting a measured quantity of solution of acid sulphite and some zinc into a flask, filling the flask with water, closing it with a caoutchouc stopper, and leaving the whole for twenty or five-and-twenty minutes. The hyposulphite thus obtained is added from a burette, first to the standard solution of copper to determine its strength, and then to a litre of the water coloured with Coupier's blue. The disappearance of the colour in each case shows the presence of unoxidized hyposulphite, and therefore the completion of the action.

E. D.

Analysis of Commercial Amorphous Phosphorus. By R. Fresenius and E. Luck (Zeitschr. Anal. Chem., xi, 63; Chem. Centr., 1872, 391).

Commercial red phosphorus usually contains ordinary as well as amorphous phosphorus, also phosphorous and phosphoric acids, and sometimes other impurities, such as sand, ash, etc. The phosphorous and phosphoric acids are washed out by water; the former is estimated by the reaction with mercuric chloride, one molecule of phosphorous acid reducing one molecule to mercurous chloride; and the two acids together are oxidised and estimated as usual. The ordinary phosphorus is dissolved out from the washed sample by carbon bisulphide, and the solution evaporated with a little iodine; the phosphorous iodide is decomposed with water and oxidised with nitric acid; and the phosphoric acid thence resulting is estimated by precipitation with ammonium molybdate and conversion into ammonio-magnesic phosphate. Lastly the red phosphorus is oxidised with nitric acid and estimated as usual. A sample analysed by the authors contained 92·63 red phosphorus, 0·56 yellow phosphorus, 1·308 phosphorous acid, 0·880 phosphoric acid, 4·622 water and impurities.

A. P.

Use of Acid Potassic Sulphate as a Flux for Metallic Sulphides and Analogous Compounds. By M. Websky (Zeitschr. Anal. Chem., xi, 121—135).

The author proposes to make an intimate mixture of equal parts by weight of the finely powdered sulphide with dry neutral potassic sul-

phate, and to moisten it with concentrated sulphuric acid in a platinum crucible (if below ·5 grm.), or in a platinum dish. After leaving it to soak for a few minutes, he covers the mass with six times its own weight of coarsely powdered acid sulphate, and applies a gradually increasing heat in such a manner as to avoid boiling over or spirting. He heats finally to dull redness till a portion of the salts begins to solidify in the fused mass. As a rule, the latter becomes clear, or shows a mottled appearance (Cu, Co, Ni) only on the application of a red heat. The different tints which the fused mass assumes on cooling are characteristic of certain elements. The cake which detaches itself for the most part readily from the platinum, is dissolved in water, if necessary, with the addition of a little sulphuric or hydrochloric acid.

Only a few elements resist at a high temperature the oxidising action of sulphuric acid. Gold remains quite unacted upon, platinum nearly so, selenium volatilises as such; sulphur volatilises or becomes oxidised; arsenic volatilises partially; mercury for the most part at a red heat. Non-volatile metallic elements become oxidised and are left as sulphates or double sulphates. Some metallic sulphates lose sulphuric acid and leave basic salts (Hg) or acid metallic oxides (Sb).

For the details of the changes observed during fusion, likewise for those on cooling or dissolving of the fused mass, we must refer to the original paper. The analytical treatment and examination of the fluxed mass, according to various special methods, presents no novelties. In order to avoid loss from the volatilisation of arsenic, it is recommended to fuse arsenides, first with a mixture of sodic hydrate and sulphur in a porcelain crucible, and to subject any residue containing only small quantities of arsenic and antimony to fusion with acid potassic sulphate. No advantage is claimed for treating in like manner any residue left from the fusion of arsenical ores with nitre and soda.

W. V.

On Marx (Goppelsroeder's) Method for estimating Nitric Acid in Well-waters by means of Indigo Solution. By J. M. van Bemmelen (Zeitschr. Anal. Chem., xi, 136—150).

Marx's method is based upon the action which a very dilute indigo solution exerts upon a dilute (centinormal) solution of potassic nitrate in the presence of double the volume of concentrated sulphuric acid. The indigo solution is added with continual shaking, and as quickly as possible, as long as decoloration takes place, and till the solution acquires a greenish tint. Goppelsroeder modified the experiment to first adding the required amount of indigo solution to the nitrate solution, and then the concentrated sulphuric acid, and claims for it greater accuracy. Van Bemmelen finds (what was pretty well known already) that the results thus obtainable vary with the quantities of nitrates present in waters, and that a fresh decoloration of the indigo-solution is obtained when fresh quantities of sulphuric acid are added, and comes to the conclusion (1) that the quantity of acid must be double that of the aqueous (both indigo and nitrate) solution; (2) that the greatest amount of indigo is used only when the proper quantity is added at once to the water before mixing it with the sulphuric acid.

If the indigo solution be added afterwards, a little more than one-half only is required. The author gives it as his opinion that the method may be used with these precautions, and that fairly accurate results may be obtained; but like the authors of the method itself, he abstained from controlling his analytical results of a number of well-waters from Arnheim, on the Rhine, by any other trustworthy method, nor does he appear to have assured himself of the purity of the sulphuric acid.

W. V.

Diphenylamine as a Test for Nitrous and Nitric Acids. By E. KOPP (Deut. Chem. Ges. Ber., v, 284).

To prepare the reagent, pure sulphuric acid is poured over a few crystals of diphenylamine, and a little water is added, whereby the temperature is somewhat raised and the crystals dissolved; the solution is then mixed with a larger quantity of pure acid. This clear colourless liquid at once produces a beautiful and very permanent blue coloration in ordinary sulphuric acid of 60° or 66 B., or chamber acid (52° B.), containing even traces of nitrous acid. The reaction is at least as delicate as that with ferrous sulphate.

The test may be rendered quantitative by comparing the coloration produced respectively by 1 c.c. of the acid to be tested, and 1 c.c. of acid containing a known amount of nitrous acid with an excess of the reagent (a solution of 1 grm. diphenylamine in 1 litre pure sulphuric acid), and adding pure sulphuric acid to one or other of the solutions until the intensity of colour is alike in both cases. Although not absolutely accurate, the method is sufficiently so for most technical purposes, and is far simpler than many of the methods ordinarily employed.

H. E. A.

Estimation of Nitric Acid. By MOHR (Zeitschr. Anal. Chem., xi, 167—169).

ACCORDING to Hager, nitrates in presence of chlorides can be determined by ignition with oxalic acid and titration of the alkaline residue. Mohr has found that sodium chloride is also decomposed by ignition with oxalic acid, and that consequently the method gives too high results when sodium chloride is present.

A. T.

The different Methods for Estimating Phosphoric Acid in presence of Iron Oxide, Alumina, Potash and Magnesia. By J. V. JANOVSKY (Zeitschr. Anal. Chem., xi, 133—167).

THE author has estimated phosphoric acid in a solution containing known quantities of the above solutions by the under-mentioned methods. The phosphoric acid was in every case weighed as magnesium pyrophosphate. 100 parts of P_2O_5 employed, gave, according to the method of:—

	a.	b.	c.
Sonnenschein	99·75	99·67	99·87
Giraud	99·64	99·51	99·68
Otto (dissolved and reprecipitated)	99·70	99·50	99·64
„	100·69	100·20	100·09
Fresenius (new)	99·59	99·55	99·61
Rose, H.	99·43	99·49	99·54
Schulze	98·42	98·26	98·18
Fuchs	97·19	96·26	96·58

The methods of Chancel and Warington are regarded by the author as inaccurate.

A. T.

Alcoholic Vapour Blowpipe. By S. RÁKÓCZY (Chem. Centr., 1872, 437).

THE apparatus consists of a sheet metal can with a screw lid, having a tube projecting from the upper part, to which is screwed a blowpipe nozzle. Alcohol being poured into the can, the lid is fitted on air tight, and a spirit-lamp placed below the can. A stream of alcohol vapour is thus forced out at the blowpipe nozzle, which may be ignited, and used as a blowpipe.

M. M. P. M.

Chemico-legal Detection of Alcohol. By KNIJPER (Chem. Centr., 1872, 440).

THE author found 22 grams of alcohol in the stomach of the dead body of a woman floating in water. The alcohol was determined by subjecting the contents of the stomach, previously neutralised with sodium carbonate, to distillation.

The brain also, 68 hours after death, smelt slightly of alcohol, and yielded 2·758 grams on distillation.

M. M. P. M.

Estimation of Acetic Acid in Wine. (Dingl. Polyt. J., ccv, 388.)

THE wine is neutralised with baryta, and the alcohol is distilled off; phosphoric acid being added, distillation is again had recourse to; all the acetic acid separated from alcohol is found in the second distillate.

M. M. P. M.

Influence of Aluminium Sulphate and Lead Acetate on the Polarisation of Sugar Solutions. By OTTO KOHLRAUSCH (Chem. Centr., 1872, 444—447).

WHEN basic lead acetate is added to a solution of raw sugar, a precipitate is formed, which of course occupies some space, and so reduces the volume of liquid contained in the marked flask in which the opera-

tion is performed. It is the object of this paper to estimate the loss of volume so occurring when solutions of aluminium sulphate and basic lead acetate, which completely precipitate one another in equal volumes, are substituted for the simple lead-salt. As all experiments were made with pure sugar, they have little practical value, since the precipitate formed consisted only of the mixed lead sulphate and basic aluminic acetate.

The author found that the addition of each 5 c.c. of a solution of aluminic sulphate containing 0·08 grm. alumina in 100 c.c., and the quantity of basic lead acetate required to precipitate it, formed a precipitate occupying 0·1 c.c. nearly, and therefore raised the polariscope by 0·1 per cent. on 100 of sugar.

C. H. G.

Testing Crude Carbolic Acid. By HAGER (Chem. Centr., 1872, 412).

FIVE c.c. of the sample are shaken with 3 c.c of a mixture of caustic potash (specific gravity, 1·34) and alcohol (of 95 per cent.); 5 c.c. petroleum benzol are then added, and the whole again shaken; after settling, the number of cubic centimeters which the lower layer of liquid has gained, gives the amount of phenol in 5 c.c. of the sample.

M. M P. M.

Formation and Detection of Hydrocyanic Acid. By ALMÉN (Chem. Centr., 1872, 439).

THE author's researches show that potassium ferrocyanide, when in solution, is decomposed at ordinary temperatures, especially if a little free acid be present, hydrocyanic acid being formed. Prussian blue is decomposed only when warmed to 40°—50°; this action is hindered, but not entirely stopped by the presence of tartrate or carbonate of potassium.

In the detection of hydrocyanic acid in a solution which has contained potassium ferrocyanide, the author recommends, after adding ferric chloride, to pass a stream of air first through the solution, and then through weak caustic soda-solution, any hydrocyanic acid present is here absorbed; but the presence of this acid, if accompanied by potassium ferrocyanide, is not proof of poisoning by means of the acid, as the potassium salt is so easily decomposed, and hydrocyanic acid thereby formed.

M. M. P. M.

Detection of Brucine, Emetine, and Physostigmine. By PANDER (Chem. Centr., 1872, 440).

1. *Brucine.*—The most delicate test is Dragendorff's modified nitric acid test. $\frac{1}{50}$ mgm. brucine, dissolved in sulphuric acid, gives, when a drop of nitric acid is allowed to come in contact with it in a watch glass, at first a rose colour, then orange, and lastly yellow. The red violet colour

which is caused by addition of tin chloride or ammonium sulphide is distinct only with not less than $\frac{1}{10}$ mgm. of the alkaloid.

Potassium iodide gives a kermes-coloured precipitate, even in a solution diluted 50,000 times. Potassium bismuth iodide gives an orange-red precipitate in a 5,000 times diluted solution. The presence of strychnine does not affect the nitric acid test, nor does caffeine interfere with the detection of brucine.

2. *Emetine.*—Sulphuric acid containing molybdic acid gives a reddish colour, speedily changing to green, even with $\frac{1}{100}$ mgm., while with $\frac{1}{150}$ mgm. emetine this reagent gives a reddish iridescence. Potassium-bismuth iodide and potassium-cadmium iodide both serve as reagents for detecting $\frac{1}{50}$ mgm. of this alkaloid in a solution diluted 25,000 times.

Brucine, if present in 10 times greater quantity than emetine, destroys the reaction with sulphuric and molybdic acids. Caffeine does not affect the tests for emetine. Brucine is easily detected in presence of emetine.

3. *Physostigmine.*—Bromine-water added to a solution of $\frac{1}{20}$ mgm. of this alkaloid 1,000 times diluted, gives a red brown colour. Calcium chloride, after a few minutes, gives a red colour, with $\frac{1}{2}$—1 mgm. physostigmine.

It requires, according to the author, $\frac{1}{100}$ mgm. (not $\frac{1}{2000}$, as stated by Vée and Leven) to produce the contracting action of this alkaloïd upon the pupil of the eye. (The experiments were tried with dogs.)

M. M. P. M.

Detection of Picrotoxin in Beer. By Blas (Chem. Centr., 1872, 441—442).

The hop bitters are removed by shaking up 6 litres of the beer, evaporated to a small bulk and previously saturated with soda, with $\frac{1}{10}$ of its volume of ether; the residue is then acidified, and on again shaking with ether, the picrotoxin goes into solution, and is obtained as an intensely bitter mass on evaporating off the ether. This mass is dried in the water-bath, taken up with alcohol acidified with one drop of acetic acid, and the filtered solution is evaporated on watch-glasses, if no distinct crystals are obtained, alcohol is added, and recrystallisation resorted to.

Picrotoxin crystals appear under the microscope like a fan, with the edges parted and somewhat cut up; they also often resemble a wheat-sheaf.

The difficulty with which picrotoxin dissolves in water and ether, its easy solubility in alcohol, its bitterness, and its action on fishes, serve as further tests for identification of these crystals as really consisting of picrotoxin.

Two fishes of about 200 grams weight are to be placed in 2 litres of water, and a portion of a solution of the crystals obtained as above is then added (this solution is made by taking up the supposed picrotoxin in alcohol, adding water, and boiling to drive off the alcohol); if it be really picrotoxin the fish soon turn on their backs and die. Lupulin has not this poisonous action on fish; 1—2 grams of hops may be boiled

in water, and poured into the jar containing the fish without affecting them: 2 grams of cocculus indicus, corresponding to 0·1 gram picrotoxin, is sufficient to kill a fish of 200 – 300 grams weight in 10 hours. At least 6 litres of the beer should be taken in applying these tests. If the residue, after shaking twice with ether as above, has a bitter taste, this points to the presence of salicin, quassin, or menyanthin. The liquid must then be precipitated with lead acetate; the filtrate freed from excess of lead, and mixed with tannic acid; the resulting precipitate warmed with alcohol and hydrated lead oxide; and the filtrate specially tested.

Another process is given by Depaire in a notice on the above paper of Blas. The beer is shaken with common salt (360 grams per litre), and filtered; the filtrate shaken twice with ether; the residue from evaporation of the ethereal solution, dissolved in alcohol; 15 c.c. water and one drop sulphuric acid added to the solution; the liquid heated for 15 minutes in the water-bath, cooled, filtered, and shaken with ether; the ethereal solution evaporated; and any crystals thus obtained recrystallised from alcohol and examined.

M. M. P. M.

The Determination of Extract in Beer or Wort. By O. Knab (Chem. Centr., 1872, 508—510).

The author observes that it is not possible to determine accurately the amount of extract in beer or wort by the specific gravity method, as the various constituents of wort increase its specific gravity unequally, and the composition of malt-extract is not constant. He finds that the best method of estimating the extract is to evaporate 10 c.c. of the fluid in a tared Liebig's drying tube, placed in an oil-bath heated to 102°, a current of dry air being passed through the apparatus.

Three samples of wort evaporated in this way yielded respectively 13·8589, 13·7900, and 14·1756 per cent. of extract; but when the percentages were deduced, by the aid of Balling's tables, from the specific gravities of the samples, the results were 14·582, 14·558, and 15·186 per cent. respectively. Further experiments showed that when dextrin is estimated by the specific gravity method, and the results are calculated by Balling's tables, the numbers are, as in the case of malt extract, higher than those obtained by the evaporation method, as described above. In the case of sugar, Balling's tables give satisfactory results.

T. B.

New Reaction of Alkalis with Tannic Acid. By V. Griessmayer (Zeitschr. Anal. Chem., xi, 43; Chem. Centr., 1872, 392).

A drop of tannic acid solution is mixed with 1 c.c. of a $\frac{1}{100}$ normal iodine solution, forming gallic acid and hydriodic acid. If now to this liquid there be added a drop of very dilute alkali, such as ammonia, or even 1 c.c. of a well-water, which exhibits a feeble alkaline reaction after the evaporation of the carbonic acid contained in it, a brilliant red colour will be produced.

A. P.

Testing of Indigo. By J. LOEWENTHAL (Zeitschr. Anal. Chem., xi, 45; Chem. Centr., 1872, 392).

THE author holds that the methods of testing indigo based on the oxidation of the sulphuric acid solution are not so trustworthy as the estimation of the amount of ash present in the sample; this he has found to vary in some cases from 4·5 per cent. in a good sample to 29 per cent.

A. P.

Technical Chemistry.

Tessié du Mothay's Method of Preparing pure Chlorine and Hypochlorites. (Dingl. Polyt. J., ccv, 359—358).

A STREAM of hydrochloric acid gas is passed into a retort containing manganese oxide and chalk, kept at a dull red heat, whereby chlorine and watery vapour are evolved; and the chlorine is passed into water, or into a chamber where dry hypochlorites are to be prepared. A stream of air being now passed into this chamber, the chlorine which had gone to form calcium chloride is set free, and is conducted (mixed with air as it is) into stoneware vessels containing a mixture of chalk and manganous oxide; manganic oxide and calcium hypochlorite are thus produced, together with calcium chloride. This mixture treated with hydrochloric acid evolves chlorine, which may be passed into the chamber where it is wanted for use. The residue in the vessel (manganous chloride and calcium chloride) heated with excess of chalk, and freed from calcium chloride by washing, gives again the original mixture, into which fresh supplies of chlorine mixed with air may be conducted.

The calcium chloride is transformed by the action of magnesium carbonate into magnesium chloride (which again yields hydrochloric acid) and calcium carbonate. The chlorine produced by this method is said to be very pure.

M. M. P. M.

New Apparatus for the Evolution of Chlorine. By A. ORLEWSKI (Zeitschr. Anal. Chem., xi, 38; Chem. Centr., 1872, 387).

THE apparatus consists of three globes, arranged horizontally, the centre one of which is twice the size of the other two, and serves as a reservoir for the manganese peroxide in lumps. This globe is connected with the left-hand globe by a syphon, passing to the bottom of each: the left-hand globe contains hydrochloric acid. The centre globe is also connected with the globe on the right, which contains sulphuric acid, and acts as a wash-bottle. The right-hand globe has a third tube communicating with a long delivery-tube passing into caustic soda, which absorbs the chlorine when not required. On heating the centre globe with a suitable gas-lamp, the hydrochloric acid syphons on

to the manganese peroxide, and a steady flow of chlorine is the result. The left-hand globe is furnished with a syphon-tube to get rid of the manganous chloride.

A. P.

Basic Calcium Carbonate in Hydraulic Cements. By A. R. SCHULATSCHENKO (Dingl. Polyt. J., ccv, 335—353).

IT has been pretty generally supposed that the hardening of hydraulic cements depends upon the formation of a highly insoluble basic calcium carbonate; in this long paper the author gives the results of his investigations:—

(1.) Analyses of various cements.

(2.) Action of carbon dioxide on dry pure calcium oxide, and testing the hydraulic qualities of the resultant product.

(3.) Burning limestones to a greater and less extent, and investigation of the residue.

(4.) Investigation of a peculiar cement from Roché's manufactory in Russia.

From all of these the author concludes that there is not in any case a basic calcium carbonate formed, and that therefore it is not upon this alleged formation that the hardening action of these cements depends.

M. M. P. M.

Cement for Glass and Porcelain. By ED. LIESEGANG (Chem. Centr., 1872, 398).

THE author recommends the following as yielding a very strong cement: ½-part of isinglass is soaked in water until well swollen, the water poured off and the isinglass dissolved in alcohol with the aid of heat; ¼-part of mastic is dissolved in ¾-part of alcohol, and added to the above solution, then ¼-part of gum ammoniacum. The solution is well shaken and evaporated to the consistence of strong glue, which solidifies on cooling. For use the cement and the articles themselves (previously well cleaned) must be warmed.

A. P.

A New Method for the Extraction of the Precious Metals from Copper Pyrites. By F. CLAUDET (Ann. Chim. Phys. [4], xxvii, 407—416).

THE author in this paper describes a method of treating the incombustible residue of pyrites from which the sulphur has been removed in the vitriol works. After pulverisation, the residues are mixed with sodium chloride and roasted in a reverberatory furnace. The roasted mass consisting principally of ferric oxide, sodium sulphate, sodium chloride, and copper chloride is next lixiviated with water rendered acid by hydrochloric acid. The insoluble ferric oxide is used for the fettling of puddling furnaces, while the lixivium which contains the copper, silver, and gold as chlorides, is precipitated by addition of a soluble iodide (or a solution of kelp), the author having found that

silver iodide is much less soluble than silver chloride in a solution of sodium chloride, and that the precipitate obtained by the addition of an iodide to the lixivium contains nearly the whole of the silver, together with the gold. This precipitate is freed from copper by hydrochloric acid, and reduced by zinc, the iodide of zinc obtained being used for the precipitation of a new quantity of silver. The copper contained in the liquor from which the gold and silver have been thus separated, is precipitated by means of metallic iron.

During 1871, 16,300 tons of residue have been thus treated in the works established at Widnes by the author and Mr. J. A. Phillips, the yield of silver being 333,242 grams (10,715 troy ounces), and that of gold being 3,172 grams (102 troy ounces).

The author proposes to extract iodine from kelp by precipitation with a salt of silver.

T. B.

Preparation of Bar Iron from Pig Iron containing Phosphorus.

By TH. SCHEERER (Chem. Centr., 1872, 443).

THE iron is puddled in the ordinary way, but with the addition of calcium chloride, or a mixture of that body with an equal weight of common salt, in the proportion of about three times the weight of the phosphorus in the pig iron. It is stated that the process of puddling is hereby so accelerated that the costs are paid by the diminished loss of iron.

C. H. G.

Decarbonisation of Iron. By STERRY HUNT (Dingl. Polyt. J., ccv, 330—331).

THIS paper calls attention to Tunner's method, in which plates of cast from $\frac{1}{2}$ to $\frac{3}{4}$ ins. thick are packed in chests with sand, and kept at a red heat for several weeks, air having free access. The impurities collect as a fusible slag, and are thus removed. The author compares this method with others, which are already well known; he lays it down that other things being equal, the iron containing least silicon will make the best malleable iron.

M. M. P. M.

Khern's Iron Furnace for use with Lignite. (Chem. Centr., 1872, 393.)

FOR the use of lignite in iron furnaces, it is necessary to have the following conditions: the carbonisation of the lignite must take place in the immediate neighbourhood, and the construction of the furnace must be of such a kind that the falling to pieces of the fuel does not disturb the smelting process. It is thought better that the peat and ore should be roasted before being placed in the iron furnace, as in that case the furnace may be much reduced in height.

A. P.

Removal of Chalk from Animal Charcoal by Acetic (Pyroligneous) Acid. By G. KNAPP (Chem. Centr., 1872, 393).

IF dilute hydrochloric and acetic acids containing 2 per cent. of acid be allowed to act on half exhausted and wholly exhausted animal charcoal, in such proportion as just to dissolve the calcium carbonate, the hydrochloric acid is found to dissolve out a part only of the calcium carbonate, and a considerable proportion of the phosphate. The acetic acid, however, does not dissolve any phosphate, or more than about 70 per cent. of the calcium carbonate. On the whole, acetic acid is preferable to hydrochloric acid, as the latter injures the power of the charcoal for decolorising. Another advantage of the use of acetic acid is that, should the charcoal after treatment not be thoroughly washed, any acetate which is left will be converted on ignition into acetone and calcium carbonate, whereas in the other case, the fused chlorine-compound forms a kind of glassy covering on the surface of the charcoal, which destroys much of its decolorising power.

A. P.

On the Refining of Sugar and the Recovery of Sugar from Molasses by Alcohol. By DR. JÜNEMANN (Chem. Centr., 1872, 475—479).

THIS paper contains working details of the various well-known processes for effecting the above objects, and depends for its interest on the data derived from experiments carried out on a working scale. As the numbers relating to these experiments cannot be condensed into an abstract, the reader is referred to the original paper.

C. H. G.

Working of Beet-root Ash. By E. PFEIFFER (Arch. Pharm. [2], cl, 97; Chem. Centr., 1872, 201).

FOR analysis of the ash, see Chem. Soc. J. [2], 1872, p 908.

The potassium chloride partly existing ready formed in the ash, and partly produced from the carbonate by addition of calcium chloride, is employed for the manufacture of nitre. The mother-liquors, after removal of the crystallisable salts, contain a large quantity of potassium sulphocyanate, together with small quantities of iodides and bromides, also of rubidium salts

W. A. T.

Improvement of Wines by Heating. By L. PASTEUR (Compt. rend., lxxv, 303—308).

THIS communication gives the result of the tasting of 24 specimens of natural wines, which had been heated to temperatures varying from 75° to 50°, a sample of the wine which had not been heated being kept for comparison. Most of the samples were heated in 1865 and 1866, although some were heated in 1869, and as late as April, 1872. The samples were tasted by seven impartial judges, whose judgments were

given secretly. The result in almost every case was that the wine which had been heated was declared superior to the unheated samples, some of which latter had turned sour and colourless. The bouquet, and in some instances the colour also, was found to be better in the heated samples. The object of the heating was in the first instance to destroy any microscopic organisms that might be present in the wine and prevent it from becoming sour. The heating must be quickly performed, and as far as possible out of contact with the air. Amongst the wines experimented on were the following:—White wine (ordinary?), Bordeaux, Chambertin, Volnay, Beaune, Pomard, Gevray-Chambertin, and Saint-Georges (Cote d'Or, 1858).

A. P.

The Prevention of Mould in Solution of Gum. By A. HIRSCHBERG (Arch. Pharm. [2], cl, 44; Chem. Centr., 1872, 492).

ROMER has recently recommended quinine for this purpose, but it does not answer. The author recommends moistening the powdered gum with alcohol, then dissolving it in the requisite quantity of water, and adding to the solution a few drops of sulphuric acid. After the deposition of the precipitated calcium sulphate, a perfectly colourless solution of gum is obtained, even when white gum has not been employed. This solution does not become mouldy.

To prevent ink from becoming mouldy, and starch-paste from turning sour, a drop or two of mustard oil may be added.

W. A. T.

Boric Acid as a Preservative for Milk and Beer. By A. HIRSCHBERG (Arch. Pharm. [2], cl, 45; Chem. Centr., 1872, 496).

THE addition of a small quantity of boric acid to milk retards the separation of cream, and the milk does not become sour when kept several days. Beer also, to which boric acid has been added, does not so quickly become "hard."

W. A. T.

The Bleaching of Rape, Poppy, and Linseed Oils. By E. PUSCHER (Dingl. Polyt. J., ccv, 390).

100 KILOS. of these oils are intimately mixed with 2 kilos. of equal parts of sulphuric acid and 96 per cent. alcohol. After 24—48 hours the oils are drawn off from the black sediment which has settled down, and further washed with a quantity of warm water.

M. M. P. M.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

VI.—*New Analyses of certain Mineral Arseniates and Phosphates.*

1. Apatite; 2. Arseniosiderite; 3. Childrenite; 4. Ehlite; 5. Tyrolite; 6. Wavellite.

By A. H. Church, Professor of Chemistry in the Royal Agricultural College, Cirencester.

Apatite.

Some perfectly transparent crystals of fluor-apatite, from one of the mines in the Spanish province of Murcia, having come into my possession, I submitted them to a careful analysis. The composition of this beautiful greenish-yellow apatite is indeed well known, but in the analyses already published, one constituent appears to have been ascertained merely by difference. In the present case the total amounts of phosphorus pentoxide, chlorine, and calcium were determined, and then the tricalcic phosphate and calcium chloride to which these results corresponded were set down, any residual calcium being calculated as fluoride. Before giving the analytical numbers, I may mention that the specific gravity of a pure crystal of the mineral was 3·25, G. Rose's determination in the case of a specimen from the same locality being 3·235 (misprinted in Dana's Mineralogy 2·235).

·584	gram	gave	·389	gram	$Mg_2P_2O_7$ $\left\{\begin{matrix}\text{(by oxalic}\\\text{method)}\end{matrix}\right\}$ = 42·63 p. c. P_2O_5.
·584	,,	,,	·564	,,	$CaCO_3$ = 38·63 per cent. Ca.
·584	,,	lost	·0006	,,	H_2O on ignition = ·10 per cent. H_2O.
·342	,,	gave	·010	,,	AgCl = ·72 per cent. Cl.
1·101	,,	lost	·003	,,	H_2O on ignition = ·27 per cent. H_2O.
·5505	,,	gave	·532	,,	$CaCO_3$ = 38·65 per cent. Ca.
·7893	,,	,,	·4296	,,	CaO = 38·87 per cent. Ca.
·096	,,	,,	·064	,,	$Mg_2P_2O_7$ $\left\{\begin{matrix}\text{(by molybdic}\\\text{method)}\end{matrix}\right\}$ = 42·67 p. c. P_2O_5.

The mean percentages, deduced from those just recorded, give, as a final representation of the constituents of this specimen of apatite, the following numbers:—

$Ca_3P_2O_8$	93·11
$CaCl_2$	1·12
CaF_2........................	4·45
H_2O	·19
Loss and undetermined......	1·13
	100·00

The percentage of tricalcic phosphate is thus shown to be nearly 1 per cent. higher than that (92·26) demanded by the formula $Ca_5(PO_4)_3F$. As the analyses were made by different experimenters in my laboratory, and with every precaution that long experience could suggest, it would seem that the discrepancy has a real existence.

Arseniosiderite.

Our knowledge of this species is very imperfect. It occurs in a bed of manganese ore at Romanêche, Macon (Saone-et-Loire), and is generally mixed with distinct particles of wad. I met, however, with a specimen of exceptional purity, and in much larger fibres than usual; and in this sample, after the separation of one or two minute nodules of black manganese, the microscope revealed no want of homogeneity. The selected fibrous crystals (of a brownish-gold hue) showed also a mere trace of manganese when examined chemically. The hardness of the specimen was quite 1·5, and the specific gravity 3·36. The following are the analytical results. The mineral, dried in vacuo, lost nothing more at 100° C.

I.	·805	gram	arseniosiderite	lost in vacuo	·0065	gram	H_2O = ·81 p.c.
	,,	,,	,,	gave	·031	,,	SiO_2 = 3·83 p.c.
	,,	,,	,,	,,	·3275	,,	As_2S_3.
	,,	,,	,,	,,	·112	,,	$CaCO_3$.
	,,	,,	,,	,,	·275	,,	Fe_2O_3.
II.	1·204	,,	,,	lost at 100°	·0997	,,	H_2O.
	1·1943	,,	,,	lost on ignition	·0943	,,	H_2O.
	1·204	,,	,,	gave	·046	,,	SiO_2.
III.	1·2535	,,	,,	lost at 100°	·007	,,	H_2O.
	,,	,,	,,	gave	·0495	,,	SiO_2.
	,,	,,	,,	,,	·51	,,	As_2S_3.
	,,	,,	,,	,,	·3425	,,	$CaCO_3$.
	,,	,,	,,	,,	·427	,,	Fe_2O_3.

Subtracting the small quantities of hygroscopic water and of silica found in the above analyses, we arrive at the following percentages:—

	I.	II.	III.
Arsenic pentoxide	39·90	—	39·83
Ferric oxide	35·83	—	35·67
Lime	15·57	—	15 98
Water................	[8 70]	8·21	[8·52]

But the water as determined by difference is obviously excessive, for when the mineral was tested for other constituents not determined above, both magnesia and potash were found. In analysis III, too, the filtrate from the calcium oxalate precipitate gave ·006 gram of $Mg_2P_2O_7$, and ·0275 gram potassium-platino-chloride, corresponding respectively to ·18 per cent. MgO, and ·47 per cent. K_2O. If we deduct these combined percentages from the 8·52 of undetermined matters in analysis III, we have the number 7 87 as representing the percentage of water in arseniosiderite. I think this is nearer the truth than the direct result of analysis II, since there may have been a minute loss of arsenic on igniting the substance. Accepting, then, this result, and the mean percentages of the other constituents, we are led to the following numbers for the centesimal composition of this species. I give them as compared with those required by the nearest formula for the mineral:

Analysis of Arseniosiderite.

	Experiment.	Theory. $4Fe_2O_3.5CaO.3As_2O_5.7aq.$
Fe_2O_3........mean	35·75	36·87
CaO ....mean	15·53	16·13
MgO	·18	—
K_2O..............	·47	—
As_2O_5........mean	39·86	39 74
H_2O..............	7 87	7·26
	99·66	100·00

The formula of arseniosiderite is thus somewhat simplified by the present analytical inquiry, becoming—

$$\left.\begin{matrix}5CaO\\H_2O\\Fe_2O_3\end{matrix}\right\}3As_2O_5.\ 3(Fe_2O_3.\ 2H_2O).$$

The latter member is already known as a distinct species under the name xanthosiderite, and, singularly enough, presents a marked resemblance to the present species in physical characters.

Childrenite.

Since 1867, when Mr. Talling furnished me with a supply of this mineral in clean and characteristic crystals, its analytical examination

has been carried on at intervals in my laboratory. The solitary analysis hitherto published had not led to any satisfactory view of the constitution of childrenite, and the necessity of further research has been long felt by mineralogists. Before giving the result of analysis, I may premise that the mineral was from the George and Charlotte mine near Tavistock, and had the specific gravity 3·22. The powdered samples did not change in weight when in vacuo over oil of vitriol, nor at 100° C. In some experiments the water was driven off by igniting the mineral in a current of pure carbon dioxide, and its quantity ascertained, not only from the loss the mineral thus suffered, but from the gain in weight of the pumice and sulphuric acid tube in which the moisture was retained. In giving the results of each analysis, their presumed value in determining the problem under investigation will be discussed.

Analysis i.

·27	gram	childrenite gave	
·006	"	SiO_2.	
·1232	"	$Mg_2P_2O_7$	= 29·84 per cent. P_2O_5 corrected for SiO_2.
·0765	"	Fe_2O_3	= 26·76 " FeO "
·0415	"	Al_2O_3	= 15·72 " Al_2O_3 "

Analysis ii.

·27	gram	childrenite gave	
·003	"	SiO_2	
·0485	"	H_2O (directly determined) = 18·16 p. c. corr. for SiO_2,	
·0415	"	H_2O (by loss) = 15·54 per cent. corr.	
·132	"	$Mg_2P_2O_7$	= 31·62 per cent. P_2O_5 corr.
·081	"	Fe_2O_3	= 27·07 per cent. FeO, corr.
·04	"	Al_2O_3	= 14·81 per cent. Al_2O_3, corr.

I consider these results, though obtained with but small quantities of the mineral, as very near to the truth. The two samples had been selected under the microscope fragment by fragment, and every visible impurity rejected. I do not think they contained more than a trace of spathic iron, while this substance was unfortunately present in some of the samples, subsequently examined and analysed, to a considerable extent, being intergrown with the childrenite crystals, and not wholly separable by mechanical means. The determination of water by loss in analysis ii. is less trustworthy than the direct determination; and this, as well as the similar observations subsequently given, will be omitted from the final calculation of the mean analytical results.

Analysis iii.

·7686 gram childrenite gave ·011 gram SiO_2, and
·1251 " H_2O (direct determination) = 16·03 per cent. H_2O, corr.

·1224 gram	H_2O (by loss)	= 15·70	per cent.	H_2O corr.
1·194 ,,	$(Ur_2O_3)_2P_2O_5$	= 30 72	,,	P_2O_5, corr.
·022 ,,	$Mg_2P_2O_7$	= 1·03	,,	MgO, corr.
·064 ,,	Mn_3O_4	= 7·74	,,	MnO, corr.
·2175 ,,	Fe_2O_3	= 25·91	,,	FeO, corr.
·127 ,,	Al_2O_3	= 16·52	,,	Al_2O_3, corr.

In this analysis, where every ascertained constituent of the mineral had been estimated, a deficiency of nearly 2 per cent. occurs, the sum of the above percentages being but 98 09. It therefore became necessary to ascertain whether the iron was rightly calculated as ferrous oxide. A determination of iron in a small portion of the same sample of the mineral was therefore made by the permanganate method, the mineral being dissolved out of contact with oxygen. ·333 gram of childrenite (SiO_2 deducted) took 25·3 cub. cent. of a standard solution of permanganate. Each cub cent. corresponding to ·0024 gram Fe, this experiment indicates the presence of ·07807 FeO in the substance taken, or 23 45 per cent. FeO.

Deducting this percentage from the total found in analysis iii, we have a residual percentage of 2·46 FeO, which corresponds to 2 73 percentage of Fe_2O_3. This result still leaves the figure 1·78 necessary to complete the 100 parts.' But the accordance of the analyses now given is, in the main, sufficient to justify us in presenting their mean results as follows, where, however, the FeO of IV is accepted throughout the series, and the residues are transformed into Fe_2O_3.

	I.	II.	III and IV.	Mean.
Ferrous oxide	26·76	27·06	23 15	23·15
Ferric oxide	—	—	2 73	3 51
Alumina	15 72	14·81	16 52	15 85
Manganous oxide	—	-	7 74	7·74
Magnesia	—	-	1 03	1 03
Water		18·16	16 03	17·10
Phosphorus pentoxide	29 84	31·62	30 72	30 65
			98·22	99·33

Before referring to the remaining analyses made on another sample of childrenite more recently received from Mr. Talling, it may be well to see how far the present results agree with those of the published analysis by Rammelsberg, and with the formula for this species which that great mineralogist suggested. In the following table I present two theoretical and two experimental sets of percentages:—

	Experiment.		Theory.	
	R.	C.	R.	C.
Ferrous oxide	30·68	26·63	29·3	26·67
Alumina	14·44	15 85	14·0	15·26
Manganous oxide	9·07	7·74	9·5	10 52
Water	16·98	17·10	18·3	16·00
Phosphorus pentoxide	28·92	30 65	28·9	31·55
Magnesia	·14	1·03	—	—
Additional O in Fe_2O_3	—	·29	—	—
	103·23	99·29	100 0	100·00

Rammelsberg's suggested formula is $8MO.2Al_2O_3.3P_2O_5.15aq.$, where M stands for Fe and Mn, and the oxygen ratio is 8 : 6 : 15 : 15. The formula I venture to suggest is $7MO.2Al_2O_3.3P_2O_5.12aq.$, which may be arranged as a combined phosphate and hydrate, thus :—

$$\left.\begin{matrix} 5FeO \\ 2MnO \\ 2H_2O \end{matrix}\right\} 3P_2O_5 + 2Al_2H_6O_6 + 4aq.$$

In justifying the proposed formula I may urge that the differences between experiment and theory are just those which might have been anticipated—$\frac{2}{7}$ of the MO present are assumed to be MnO, and $\frac{5}{7}$ FeO—experiment shows the replacement of the latter oxide by the former to have been accompanied by a second replacement by MgO. Thus there is a deficiency in the MnO found, but if we translate the magnesia percentage (see analysis VI further on) into its equivalent of MnO, this deficiency is just supplied. The experimental percentage of water is 1 per cent. too high, and that of phosphorus pentoxide nearly as much too low; but if we compare the percentages deduced from the best of the three analyses already given, where $\frac{3}{4}$ gram. of childrenite was used, the accordance is nearer, since experiment there gave 16·03 per cent. H_2O and 30·72 per cent. P_2O_5, theory requiring 16·00 and 31·55 respectively. Nor is it difficult to appreciate the chances of error in the determination of these two compounds in so peculiar a substance as childrenite. Other considerations in support of the new formula I need not urge, as they will be apparent to those chemists who have studied the constitution of the native phosphates. But I must here cite some additional analyses of childrenite, in order to indicate one source of error in its analysis, namely, an admixture with chalybite, causing an excess in the percentage of FeO, and a deficiency in that of P_2O_5.

Results of additional Analyses.

	Amount taken.	Per cent. H_2O.	Per cent. FeO.	Per cent. Al_2O_3.	Per cent. P_2O_5	Per cent. MnO	Per cent. MgO.	Per cent. CO_2.
V ...	·677 gram	15·83 direct / 15·82 indirect	31·65	16·66	—	—	—	—
VI ..	·551 „	—	31·28	16·63	27·73	7·38	1·86	2·54 = 6·69 $FeCO_3$
VII .	·486 „	16·42 indirect	—	—	30·58	—	—	—

Analyses V and VI are given mainly in order to show the effect of an admixture of chalybite in diminishing the phosphorus pentoxide and water, and increasing the ferrous oxide. The manganous oxide determination previously given is confirmed by the number obtained in VI; while the higher percentage of MgO in this analysis may perhaps be due to the intruding chalybite, which, when separately examined, was found to contain some quantity of that base. The sample used in analysis VII was nearly free from impurities, and the results accord well, so far as they go, with those of the first four analyses.

Ehlite.

From time to time I have met with a phosphate of copper presenting the closest resemblance to the rare mineral cornwallite, but in which there is a mere trace of arsenic pentoxide; it appears to occupy the same place amongst the hydrated cupric phosphates that cornwallite occupies amongst the arseniates. It may be distinguished by the radiating fibro-crystalline structure revealed when the botryoidal globules are fractured, and perhaps by a somewhat bluer hue in its green colour. It sometimes presents a slightly drusy surface, and occurs either investing quartz, or in reticulated chains of globules cementing silicious fragments. Its specific gravity is about 4·23, but one piece weighing nearly 4 grams gave 3·911. Before the blowpipe in a closed tube, it gives off water without decrepitation, becoming a blackish olive-green; it fuses to a grey-black bead in the forceps. Its colour lies between grass-green and verdigris-green. In the following table I present the analytical details of the examination of three specimens of this mineral.

Analysis I was made in 1867 with an old Cornish specimen which then came into my possession; II with another specimen of similar character subsequently obtained; and III represents the results of the analysis of specimens lately forwarded by Mr. Talling.

	I.	II.	III.
Substance taken	·462	·391	·62
H_2O in vacuo..........	—	none	·0005
H_2O at 100°	—	·0015	·0025
H_2O at a red heat......	·0365	·036	·056
CuO	·293	·26	·409
$Mg_2P_2O_7$	·141	·145	—
As_2S_3................	·0115	trace	trace
SiO_2	·02	·0005	·0055
Fe_2O_3................	·0063	none	none

The species does not lose anything more than traces of water in vacuo or at 100° C. When these traces and the silica are deducted, the three analyses give the following percentages:—

	I.	II.	III.
H_2O	8·25	9·26	9·16
CuO	66·29	66·84	66·88
P_2O_5	20·38	23·73	[23·96]
As_2O_5........	2·42	trace	trace
Fe_2O_3........	1·42	—	—
	98·76	99·83	100·00

These numbers correspond to those demanded by the formula $5CuO.P_2O_5.2H_2O$; which may be written $Cu_3P_2O_8.2CuH_2O_2$ + aq., thus representing cornwallite, $Cu_3As_2O_8.2CuH_2O_2$ + aq., in the phosphate series. It is the ehlite of Breithaupt, and the pseudo-malachite var. A of Dana. The theoretical percentages are:—

$3H_2O$	9·10
$5CuO$	66·98
P_2O_5	23·92
	100·00

Tyrolite.

This very beautiful mineral is clearly distinguished from all other arseniates of copper, save, perhaps, chalcophyllite, by its talc-like softness, pearly lustre, and flexibility. It decrepitates violently in the closed tube, owing to the interstitial moisture retained between its laminæ, and swells up greatly, finally melting into a grey globule when heated before the blowpipe. It contains calcium carbonate as an essential constituent, not as an accidental impurity. This point may be proved by the examination of the pure uniform bluish-green laminæ of the mineral under the microscope. Both in ordinary and in polarized light, these are seen to be perfectly homogeneous and equally coloured

and transparent in all parts; and when a drop of acid is allowed to creep between the glass slide and the thin cover, so as to dissolve a plate of tyrolite under the microscope, then the bubbles of carbon dioxide disengaged appear with perfect regularity. The calcium carbonate, too, in all the analyses made, obviously exists in a definite, atomic, and constant proportion. Only one analysis, however, has hitherto been published, though the kindness of Mr. Bryce Wright now enables me, through his liberal gift of a choice fragment of tyrolite, to present some further results. I presume, from the habit of the crystals and from the accompanying minerals, that the specimen analysed is from the Libethen locality. Its specific gravity was 3·162.

The following are the details of the analysis of tyrolite:—

	I.	II.
Substance	·299	·4585
H_2O lost in vacuo	·01	·024
H_2O lost at 100°	·01	·011
$CaCO_3$	·035	·0505
CuO	·142	·212
$Mg_2P_2O_7$	—	·205

The analyses agree well, but No. II is of course more satisfactory, since a more adequate quantity of material was there employed. Deducting the water lost in vacuo and at 100° (6·7 per cent. in I, and 7·2 per cent. in II), the percentages of the other ingredients will stand thus:—

	Experiment. I.	Experiment. II.	Theory. $5CuO,As_2O_5,4H_2O.CaCO_3$.
CuO	50·90	50·06	50·35
As_2O_5	—	29·29	29·13
$4H_2O$	—	[8·73]	9·12
$CaCO_3$	12·55	11·92	11·40
		100·00	100·00

The formula I propose differs in but one particular from the expression adopted by Brooke and Miller, and that is in the amount of water. Rammelsberg excludes the calcium carbonate as an intruding ingredient—an exclusion for which the singularity of such an occurrence as a carbonate-arseniate offers some warrant, but which the physical and chemical properties of tyrolite do not countenance. As to the true proportion of water in this mineral, I cannot hesitate for a moment in regarding all the water lost *in vacuo* over oil of vitriol as merely accidental, while the further loss at 100° ought probably to be regarded in a similar light. If some of the largest laminæ of tyrolite be examined under the microscope, the water may be seen to be irregularly dispersed between the pearly faces of the crystals, and when these

have been dried *in vacuo* and at 100° their colour and transparency are not altered, though the interstitial water has disappeared. The $4H_2O$ assumed in the formula now proposed exactly suffices for the hydration of the $2CuO$ uncombined with any acid constituent, and has so far an argument in its favour. When, too, the powdered tyrolite dried at 100° is heated in a closed tube it loses water and blackens simultaneously, the cupric hydrate becoming the oxide.

The new formula for tyrolite may be expressed—

$$3CuO.As_2O_5;\ 2(CuO.H_2O);\ CaO.CO_2 =$$
$$Cu_3As_2O_8;\ 2CuH_2O_2;\ CaCO_3.$$

In the mineralogical notation this becomes (where the barred symbols signify two atoms, and the atomic weights are those used in this paper)—

$$5\dot{\mathrm{Cu}}\overset{\cdot\cdot\cdot\cdot\cdot}{\overline{\mathrm{As}}},\ \dot{\mathrm{Ca}}\ddot{\mathrm{C}},\ 4\overline{\mathrm{H}};\ \text{or}\ 3\dot{\mathrm{Cu}}\overset{\cdot\cdot\cdot\cdot\cdot}{\overline{\mathrm{As}}},\ 2\dot{\mathrm{Cu}}\overline{\mathrm{H}},\ \dot{\mathrm{Ca}}\ddot{\mathrm{C}}.$$

Brooke and Miller's formula becomes

$$5\dot{\mathrm{Cu}}\overset{\cdot\cdot\cdot\cdot\cdot}{\overline{\mathrm{As}}},\ \dot{\mathrm{Ca}}\ddot{\mathrm{C}},\ 10\overline{\mathrm{H}},$$

and Rammelsberg's—

$$5\dot{\mathrm{Cu}}\overset{\cdot\cdot\cdot\cdot\cdot}{\overline{\mathrm{As}}},\ 9\dot{\overline{\mathrm{H}}};\ \text{or}\ 3\dot{\mathrm{Cu}}\overset{\cdot\cdot\cdot\cdot\cdot}{\overline{\mathrm{As}}},\ 2\dot{\mathrm{Cu}}\dot{\overline{\mathrm{H}}},\ 5\dot{\overline{\mathrm{H}}}.$$

If by analogy with the chloro- and fluo-phosphates we assume tyrolite to contain a carbonate-phosphate, it may be expressed thus:—

$$\left.\begin{matrix}3CuO\\ CaO\end{matrix}\right\}\begin{matrix}P_2O_5\\ CO_2\end{matrix};\ 2(CuO.H_2O).$$

Wavellite.

I give the following analytical results merely as a contribution towards the chemistry of wavellite. The quantity of constitutional water in this mineral remains a matter of doubt. Owing to its peculiar fibrous structure, the species is hygroscopic, and the analysis usually quoted exaggerates the moisture. The obscurity attached to the mineral is further increased through the presence of fluorine. The specimens analysed in my laboratory were of singular purity, and came from one of the localities in the county of Cork.

1·032 gram	lost in vacuo	·0215 gram	H_2O	= 2·08	p. c.	H_2O.
1·0105 „	„ at 100° C.	·0015 „	„	= 0·14	„	H_2O.
1·0090 „	„ at 200° C.	·228 „	„	=22·14	„	H_2O.
·405 „	gave	·042 „	K_2SiF_6	= 2·09	„	F.
1·0735 „	„	·002 „	SiO_2	= 0·19	„	SiO_2.
„ „	lost at 100° C.	·0245 „	H_2O	= 2·28	„	H_2O.
1·049 „	„ at dull redness	·2785 „	H_2O	=26·45	„	H_2O.
„ „	gave	·3900 „	Al_2O_3	=37·18	„	Al_2O_3.
„ „	„	·525 „	$Mg_2P_2O_7$	=32·00	„	P_2O_5.

It will be seen that the specimens analysed lost about 2 per cent. of water *in vacuo* over sulphuric acid, and that they suffered scarcely any further loss at 100°. It may fairly be assumed that the water thus lost is accidental, and the percentages have therefore been calculated on that assumption.

Analysis of Wavellite dried at 100° *C.*

Water..............	26·45	22·15 lost at 200° C. 4·30 lost at low redness.
Alumina............	37·18	
Phosphorus pentoxide.	32·00	
Silica..............	·19	
Fluorine............	2·09	
Lime and ferric oxide.	traces	
Loss	2·09	

As the fluorine is probably under estimated, I have not calculated it into its equivalent of aluminium fluoride, though it can scarcely be doubted that the mineral really is an aluminium fluo-phosphate. The "loss" above can hardly be water, but should be set down, I conclude, as partly fluorine and undetermined bases. If this point be conceded, the water in wavellite will be but 11 molecules instead of 12, while the primary formula of the species (neglecting the fluorine substitution) becomes $3Al_2O_3.2P_2O_5.11H_2O$, an expression which may be better developed as—

$$2Al_2P_2O_8 . Al_2H_6O_6 . 8aq ;$$

and which demands the following percentages:—

Al_2O_3	39·07
P_2O_5..............	35·90
H_2O..............	25·03
	100·00

It is true that the alumina found by experiment was nearly 2 per cent. too low, but this difference may be due to a partial replacement of that base by ferric oxide and other undetermined constituents. So the phosphorus pentoxide, as determined, is less by almost 4 per cent. than that demanded by theory, yet here the presence of fluorine accounts for the deficiency. If the water lost by the mineral at a dull red heat be tested for hydrofluoric acid, the presence of that compound is easily recognised, and thus the slight apparent excess of water in the analysis is explained. The fluorine will also diminish the silica remaining after treatment of the mineral with an acid, and so the loss of 2 per cent. is partly accounted for.

VII.—*On the Condition of the Hydrogen Occluded by Palladium, as indicated by the Specific Heat of the Charged Metal.*

By W. Chandler Roberts, Chemist of the Mint, and C. R. A. Wright. D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

Graham's researches "on the relation of palladium to hydrogen" led to the conclusion that the absorbed hydrogen exhibits decided metallic properties, and that the palladium with its occluded hydrogen is an alloy. As the specific heats of alloys always approximate to the means of those of their constituents (Kopp), it was thought that by determining the specific heat of the alloy and that of the original palladium, the specific heat of the occluded hydrogen could be calculated; it was further anticipated that this value would be somewhere near 6·6, in accordance with Dulong and Petit's well-known generalisation.

Palladium wire and foil, also palladium-gold alloy (containing 20 per cent. of gold) in the form of wire, were charged with hydrogen by making the metal to be charged the negative pole of a voltaic battery electrolysing acidulated water. The charged metal was well washed with water and then with alcohol, and then heated to a temperature close upon 100°; when the palladium was completely saturated with hydrogen, a slight disengagement of gas took place at 100°, but this was observed only when the occluded gas exceeded 60 c.c. at 0° and 760 mm. per gram of palladium. In the few experiments in which a further disengagement took place on repeatedly heating to 100° in the course of the determinations, the small quantity of gas thus expelled was collected and allowed for.

The specific heat between 15° and 100° of the charged palladium was then estimated by plunging the substance heated to near 100° into a calorimeter, the results being calculated by means of the following formula:—

$$S = \frac{W}{w + w'} \cdot \frac{t' - t}{T - t'} \ldots\ldots\ldots \quad \text{(No. 1.)}$$

where S = the specific heat of the charged metal,

W = the water-equivalent of the calorimeter in grams,

w = the weight of palladium,

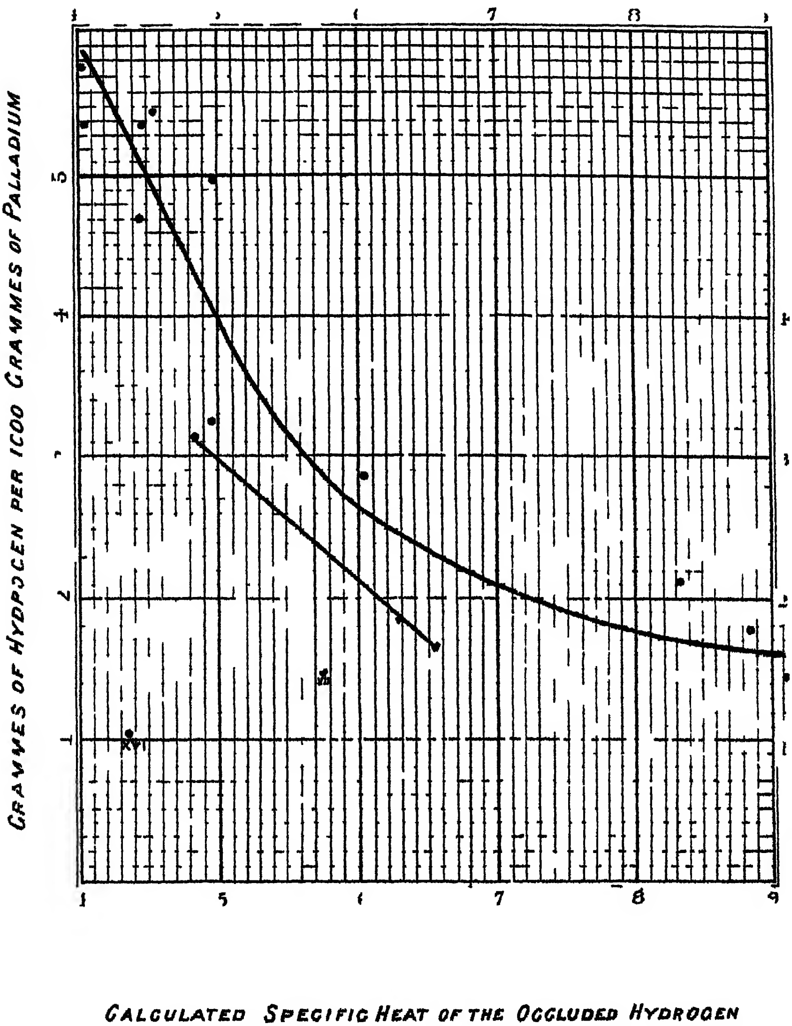
w' = the weight of hydrogen occluded,

T = the initial temperature of the charged palladium,

t = the initial temperature of the calorimeter,

t' = the final temperature of the calorimeter, corrected, when necessary, for atmospheric influences, radiation, &c.

CURVE DEDUCED FROM EXPERIMENTS ON THE SPECIFIC HEAT OR HYDROGEN OCCLUDED BY PALLADIUM



The specific heat between $-10°$ and $+15°$ was similarly calculated by the same formula, the charged palladium being cooled down to close upon $-10°$ by an alcohol-bath immersed in a freezing mixture of calcium chloride and pounded ice.

To determine the value of T, a thermometer was enclosed, together with the coil, in the heating or cooling apparatus, a bath of boiling distilled water being used for the determinations between 15° and 100°. In the earlier experiments Regnault's form of apparatus (*Ann. Chem. Phys.* [3], lxxiii, 20) was employed, but it was found that the errors arising from atmospheric cooling with his arrangement were greater than those with the one to be immediately described. With compact blocks of substance probably this would not be the case, but with the spirals of wire used, errors of considerable magnitude were often introduced by employing Regnault's form of apparatus.

A thin test-tube, provided with a loosely fitting cork and containing the charged palladium, was heated or cooled in the bath employed. It was found that a thermometer immersed in the tube so that the centre of the coil was outside the bulb of the thermometer, became stationary in less than 15 minutes after immersion in the bath; a much longer time than this, however, was allowed in each experiment. When a boiling water bath was employed, the thermometer became stationary at 0·50° below the temperature of the water. The neck of the tube was then grasped by a suitable holder, the cork withdrawn, and the coil rapidly transferred to the calorimeter, the time required for transference being from one to two seconds. It is true that a small amount of atmospheric cooling would be produced by this mode of operation; but in the short time required this cooling would probably not extend beyond the outside of the walls of the test-tube; whilst in Regnault's form of apparatus, the whole spiral coil being exposed to the air during its transference from the heating apparatus to the calorimeter, as previously stated, the error thus produced was often considerable.

The temperatures t and t' were estimated by a thermometer which could easily be read to $\frac{1}{50}$ degree centigrade. Two calorimeters were employed: one made of glass and having an outside jacket filled with dry cotton-wool loosely packed, so as to diminish errors from atmospheric action; the equivalent in grams of water of this calorimeter, together with the thermometer and stirrer, was found, as the mean of a number of concordant experiments, to be 113·3 when containing 100 grams of water. The other calorimeter was made of brass, polished outside, and supported by cross threads within an outside brass vessel, the internal surface of which was also highly polished; the water equivalent of this calorimeter was found, from the mean of several experiments, to be 85·8, when containing 200 c.c. of benzene measured at 15°, the equivalent calculated from the specific heats of brass, benzene,

&c. (Regnault, Kopp), being 85·9. It was ascertained that no evolution of hydrogen took place when the charged coils were immersed either in water or in benzene.

After the determinations of the specific heat of the charged palladium were completed, the quantity of hydrogen occluded was estimated by heating in the vacuum of a Sprengel pump, and collecting and measuring the gas expelled.

In some experiments the palladium was charged to saturation, or nearly so, by the battery, and the estimations were then made; in others only a partial charge was thus communicated; in others the metal was charged to saturation by the battery, and then a portion of the occluded gas was again expelled by heat before making the determinations.

The following table indicates the character of the numbers obtained, and the divergence in the results exhibited in consecutive experiments:—

Weight of palladium employed (w)	15·800	grams
Water-equivalent of calorimeter, &c. (W)	113·3	"
c.c's. at 0° and 760 mm. of occluded hydrogen	373·0	c.c.
Weight of ditto (w')....................	0·0333	"

	A.	B.	C.	D.
Initial temperature of calorimeter (t)......	18·50	19·10	18 71	19·08
Final " " (t')	19·37	20·95	19 58	19·94
Temperature of charged palladium (T)	99·50	99 50	99·50	99·50
Ratio $\frac{t'-t}{T-t'}$...........................	·01086	·01082	·01088	·01081
Specific heat of charged palladium between 15° and 100°	0·0777	0·0775	0·0779	0·0774
Average................ 0 0776				

It is hence evident that the errors of observation, &c., do not amount to such a quantity as materially to affect the conclusions drawn from the mean of several observations. It must be observed that in many of the experiments detailed below, corrections for atmospheric action were dispensed with by making one determination with the temperature of the calorimeter rather below that of the air, and then making consecutive experiments with the heated wire until the temperature of the calorimeter was as much above that of the air at the close of the last experiment as it was below it at the commencement of the first one. The *mean result* of the several determinations is thus unaffected by errors from radiation, &c.; but the earlier experiments show an excess, and the later ones a deficiency, when compared with the mean, owing to the errors from radiation, &c., increasing the former values and diminishing the latter.

The following numbers were obtained in sixteen experiments, in each of which at least duplicate determinations of the value of the ratio $\frac{t'-t}{T-t'}$ were made; three determinations being the normal number, and in some cases four, five, or even more:—

Experiment I.—New coil of annealed palladium wire, $\frac{1}{50}$ inch diameter, charged to saturation by battery (1st charge).

Experiment II.—Same coil, partially charged by battery (2nd charge).

Experiment III.—Same coil, charged to saturation (3rd charge).

Experiment IV.—Same coil, charged to saturation, and then partially discharged by heating (4th charge).

Water-equivalent of calorimeter........ 113·3 grams.
Weight of palladium .... 15·80 „

	I.	II.	III.	IV.
Volume at 0° and 760 mm. of occluded hydrogen	955 c.c.	316	880	373
Weight of ditto in grams	0·0853	0·0282	0·0786	0·0333
Value of ratio $\frac{t'-t}{T-t'}$	·01167 ·01167 ·01176	·01048 ·01057 ·01060 ·01061 ·01072	·01173 ·01186 ·01187 ·01199	·01081 ·01082 ·01086 ·01088
Average	·01170	0·1060	·01186	·01084
Specific heat between 15° and 100° of charged palladium..................	·08345	·07586	·08463	·07757

Experiment V.—Another coil of palladium wire, $\frac{1}{50}$ inch diameter, charged to saturation by battery (1st charge).

Experiment VI.—Same coil, saturated and partially discharged by heat (2nd charge).

Experiment VII.—Same coil, partially charged by battery (3rd charge).

Experiment VIII.—Same coil, saturated (4th charge).

Experiment IX.—Same coil, saturated (5th charge).

Water-equivalent of calorimeter .... 85·8 grams.
Weight of palladium .... 29·46 „

	V.	VI.	VII.	VIII.	IX.
c.c. of hydrogen at 0° and 760mm......	1938	1058	490	1782	1556
Weight of ditto	0 1730	·0945	·0437	·1591	·1389
Value of ratio $\frac{t'-t}{T-t'}$	·0285 ·0286 ·0289	·0259 ·0260 ·0265	·0235 ·0236 ·0237	·0279 ·0285	·0275 ·0278 ·0279 ·0285
Average	·0287	·0261	·0236	·0282	·0279
Specific heat between 15° and 100° of charged palladium	·08310	·07577	06863	·08168	·08087

Experiment X.—Annealed palladium foil, 0·168 gram to the square centimeter, partially charged by battery (1st charge).

Experiment XI.—Ditto, fully charged (2nd charge).

Experiment XII.—Ditto, charged to saturation and partially discharged by heat (3rd charge).

Water-equivalent of calorimeter.... .. 85·8 grams.
Weight of palladium.................... 15 045 „

	X.	XI.	XII.
cc. of hydrogen at 0° at 760 mm.	244	923	486
Weight of ditto	·0218	·0824	·0434
Value of ratio $\frac{t'-t}{T-t'}$	·01267 ·01272 ·01291	·01477 ·01498 ·01501 ·01501	·01333 ·01347 ·01368 ·01392
Average...........................	·01277	01494	·01360
Specific heat between 15° and 100° of charged palladium	·07273	·08174	·07731

From the determinations of the specific heat of palladium charged with hydrogen, the specific heat of the occluded hydrogen is calculated by the formula—

$$x = \frac{(w + w')s - w\,s'}{w'} \ldots\ldots\ldots\ldots \quad \text{(No. 2.)}$$

where w and w' are the weights of palladium and hydrogen respectively—

s the specific heat of the charged metal,
s' that of the palladium itself (uncharged);

the applicability of the formula being of course dependent on the assumption that the palladium and hydrogen both retain in the charged

metal the specific heats that they would otherwise possess if not associated; *i.e.*, that the charged palladium is, as Graham's experiments indicated, *an alloy*.

The determinations of the specific heat of the palladium required for this mode of calculation were made in precisely the same way as those of the charged metal, formula No. 1 being employed, the value of w' being $= 0.$: it was thus found, as might be expected *à priori*, that the specific heat of the palladium varies with each successive charging and discharging; the metal becomes more porous and spongy, the specific heat becoming higher; thus the following values were obtained between 100° and 15° and between + 15° and − 10°.

Between 15° and 100°—

(A.) Annealed palladium, uncharged.

(B.) Annealed palladium, charged once to saturation and discharged by heat.

(C.) Annealed palladium, charged three times to saturation and discharged by heat.

(D.) Annealed palladium, charged four times to saturation and discharged by heat.

Between + 15° and − 10°:

(E.) Palladium, charged four times and discharged by heat.

	Between 15° and 100°.				−10° and +15°.
	A.	B.	C.	D.	E.
Weight of palladium..........	15·80	29·46	15·80	29·46	29·46
Water equivalent of calorimeter	113·3	85·8	113·3	85·8	85·8
Values of ratio $\frac{t'-t}{T-t'}$	·00814 ·00814 ·00827 ·00830 ·00843	·02042 ·02056 ·02058 ·02003	·00833 ·00840 ·00848	·02060 ·02064 ·02065 ·02065 ·02065 ·02081	·02012 ·02019 ·02014 ·02053
Average	·00826	·02062	·00840	·02067	·02032
Specific heat of palladium*	·05921	·06007	·06022	·06022	·05918

It hence appears that the specific heat of palladium, like that of the charged metal, is higher between 15° and 100° than between + 15° and − 10°; thus—

D gives between 15° and 100° .... ·06022

E gives between + 15° and − 10° .... ·05918

* Regnault obtained the value ·05928 as the specific heat of palladium between 98° and 14°.

experiments D and E being made with the same coil under the same conditions.

The specific heat between 15° and 100° of the palladium increases with the increasing porosity of the metal produced by successive charging and discharging. As it is impossible to say whether the alteration in the specific heat takes place at the entrance or exit of the hydrogen, the following mean values are taken as the specific heat of the palladium for the 1st, 2nd, 3rd, and 4th charges respectively.

Observed specific heat.		Mean values taken.	
Annealed palladium	0·05921	For 1st charge	0·05964
Ditto after once charging and discharging	0·06007		
		„ 2nd „	0·06011
„ „ „			
		„ 3rd „	0·06019
Ditto after three times ditto ..	0·06022		
		„ 4th „	0·06022
Ditto „ four times ditto	0·06022		

There is therefore a slight uncertainty in the actual value of the specific heat of the palladium itself, which makes a corresponding difference in that of the hydrogen deduced from the specific heats of the charged palladium and the uncharged metal; the error from this source, however, does not exert any marked influence on the general character of the results.

From the preceding data the specific heat between + 15° and 100° of the hydrogen occluded in the first twelve experiments is calculated as follows:—

	Number of Experiment.					
	I.	II.	III.	IV.	V.	VI.
Weight of palladium (w)	15·80	15·80	15·80	15·80	29·46	29·46
Ditto of occluded hydrogen (w')	·0853	·0282	·0786	·0333	·1730	·0945
Specific heat of charged palladium (s) .	·08345	·07586	·08163	·07757	·08310	·07577
Number of charge..................	1	2	3	4	1	2
Specific heat of palladium alone (s') ..	·05964	06011	·06019	·06022	·05961	·06011
Ditto of occluded hydrogen........	4·49	8·87	4·99	8·31	4·08	1·95
Grams of hydrogen per 1,000 of palladium	5·39	1·79	4·98	2·11	5·86	3·21

	Number of Experiment.					
	VII.	VIII	IX.	X.	XI	XII.
Weight of palladium (w)	29·46	29·46	29·46	15 015	15 015	15 045
Ditto of occluded hydrogen (w')	0137	1591	1389	0218	0824	·0434
Specific heat of charged palladium (s) .	·06563	08168	·08087	07273	08174	·07734
Number of charge	3	4	5	1	2	3
Specific heat of palladium alone (s') ..	06019	06022	·06022	05961	06011	06019
Ditto of occluded hydrogen	5 76	4 06	4·16	9 10	4 58	6 02
Grams of hydrogen per 1,000 of palladium	1·18	5·10	4 69	1 45	5·17	2 88

If these results be graphically represented with the specific heats of hydrogen as abscissæ and the quantities of hydrogen per 1000 of palladium as ordinates, a series of points is obtained which, with one exception, lie within a small distance from a *mean curve;* the point which does not come near this curve is that deduced from Experiment VII, where a partial charge was communicated by the battery. It is inferred from this that the differences noticed between the results actually obtained and the mean curve are not improbably due to irregularity in the distribution of the hydrogen throughout the palladium. In Experiment VII the abnormal result noticed is just that which would be produced if a part of the wire were highly charged with hydrogen and the rest but little charged; a result extremely likely to be produced by the mode of charging. Where the smaller charges were obtained by saturating the wire and then expelling part of the charge by heat, there is a greater chance of uniformity in the distribution of the hydrogen, and accordingly the points approximate more closely to the mean curve. On the other hand, the points obtained from Experiments II and X, when partial charges only were communicated by the battery, lie near to the mean curve. It is noticeable that in these cases thinner wire than that employed in Experiment VII, and foil were respectively used, and hence the chances in favour of uniform distribution of hydrogen are greater than in Experiment VII.

Experiment XIII.—The charged palladium wire employed in Experiment VIII was also used in the following determination of the specific heat of the charged metal between $-10°$ and $+15°$.

Water-equivalent of calorimeter	85·8	grams.
Weight of palladium	29·46	„

c.c. of hydrogen at 0° and 760 mm.	1782
Weight of ditto	0·1591
Values of ratio $\frac{t'-t}{T-t'}$	·0272 ·0277 ·0281
Average	·0277
Specific heat between − 10° and + 15° of charged palladium	·08046

It hence appears that the specific heat of the charged palladium between 15° and 100° is perceptibly higher than that between + 15° and − 10°; thus—

Experiment VIII.—Between + 15° and 100° ...... ·08191
Experiment XIII.—Between + 15° and − 10° ...... ·08046

these two values being obtained *with the same charge.*

Calculating [by formula 2], the specific heat of the occluded hydrogen, the value 3·98 is obtained, whence it would appear that the specific heat of occluded hydrogen is slightly lower between − 10° and + 15° than between 15° and 100°; thus Experiments VIII and XIII were made with the same charge, and gave the numbers—

Experiment VIII.—Between 15° and 100°............ 4·06
Experiment XIII.—Between + 15° and − 10°........ 3·98

The difference observed in these two cases, however, is so small that it may easily be due to errors of experiment; so that not improbably the specific heat of the occluded hydrogen, like that of the free gas, is independent of the temperature.

Experiment XIV.—Graham's researches have shown that the occlusion of hydrogen by palladium causes an extension in the length of the wire used, which is followed by a *permanent retraction* of an almost equal amount when the hydrogen is expelled. Alloys of palladium and silver, or gold, containing 20 per cent. of the other metal, on the other hand, increase in length when charged with hydrogen to an extent double that exhibited by pure palladium, and on expulsion of the hydrogen return to their original dimensions without suffering any permanent retraction in length. The following experiments were instituted in order to ascertain if this property of such alloys is associated with any difference in the specific heat of the occluded hydrogen. A spiral coil of wire of palladium-gold alloy, containing 20 per cent. of the latter metal, was charged by the battery, and examined in precisely the same way as the palladium coils above described. The following numbers were obtained:—

Experiment XV.—Alloy charged with hydrogen to saturation.

Experiment XVI.—Alloy charged to saturation and partially discharged by heat.

Experiment XVII.—Alloy partially charged by battery.

Water-equivalent of calorimeter	85·8 grams.
Weight of alloy	9·81 „
Palladium contained in alloy............	7·848 „

	XIV.	XV.	XVI.
c.c. of hydrogen at 0° and 760 mm.	275	144	92
Weight of ditto	·0245	0129	·0082
Values of ratio $\frac{t'-t}{T-t'}$	0754 ·0759 ·0782 ·0784	·0728 0729 ·0735	·0671 ·0674 ·0678
Average	·0770	·0731	·0674
Specific heat of charged alloy between 15° and 100°....................	·06718	·06385	·05889

The alloy itself gave the following numbers after once charging and discharging :—

Weight of alloy	9·81 grams.
Water-equivalent of calorimeter	85·8 „
Values of $\frac{t'-t}{T-t'}$	·00625 ·00630 ·00634 ·00640
Average	·006325
Specific heat between 15° and 100° of alloy	·05533

Hence the following values for the specific heat of the occluded hydrogen are calculated :—

	XIV.	XV.	XVI.
Specific heat between 15° and 100° of occluded hydrogen	4·82	6·55	4·34
Grams of hydrogen per 1,000 of palladium........................	3·12	1·64	1·04

If these three results be graphically represented on the same scale as the former values, it is found that Experiment XVI, where the wire was

partially charged by the battery, gives (like Experiment VII) an utterly abnormal result, whereas Experiments XIV and XV yield two points that appear to be situated on a curve *parallel to that deduced above from palladium alone.* It would naturally be expected that the presence of the gold in the alloy would modify the relations of the palladium to the hydrogen, and would consequently tend to shift the curve to another and probably parallel position.

The results obtained with the palladium-gold alloy therefore corroborate those obtained with pure palladium, and taking them into account with the abnormal results obtained in Experiments VII and XVI, lead to the conclusion that the main cause of the variations from the mean curve noticed in the other experiments is the irregular distribution of the hydrogen through the palladium.

The consideration of the foregoing results seems to point to one or other of the following conclusions:—

(1.) The highest values being obtained where the lowest charges of hydrogen are occluded, it might be supposed that the hydrogen first taken up is in a quasi-liquid condition; for, as is well known, the specific heat of bodies in the liquid state is much higher than that when in the gaseous or solid form. The product of the combining number of bromine and its specific heat in the liquid state is close upon 9, whence it might be surmised that the specific heat of liquid hydrogen would be about 9, thus giving the same product. The later portions of hydrogen taken up might be considered to be in a condition more approaching that of a gas, and having consequently a much less specific heat than the quasi-liquefied portions first taken up.

The numbers obtained above do not appear to indicate any marked break or sudden fall from a high to a low value for the specific heat of the occluded hydrogen; hence the above explanation would tend to indicate *a continuity between the quasi-liquid and quasi-gaseous states* in which the hydrogen is considered to exist in the lower and higher portions of a saturating charge respectively.

Or (2), the fundamental assumption that in the charged palladium the metal and the hydrogen retain their original specific heats is perhaps untenable; in other words, palladium-hydrogenium, contrary to Graham's conclusions, is *not* an alloy but approximates more to the nature of ordinary solutions of gases in liquids. The researches of Marignac on hydrochloric acid solutions, for instance (*Phil. Mag.* [4], xli, 134) (some of whose results we have repeated and verified), indicate that the water and hydrogen chloride do not retain their original specific heats: for the specific heat of a given solution of hydrogen chloride in water is always such that a given weight of such solution parts with *less* heat in cooling through a given range of temperature than would be lost by the water contained in the solution in

cooling through the same range, *i.e.*, the specific heat of the hydrogen chloride must be *negative* if that of the water remain unity.

It is curious that in the case of hydrochloric acid the specific heat of a solution is *less* than that deducible from the specific heats of the constituents in the liquid and gaseous states respectively, whilst in the case of solution of hydrogen in palladium, the specific heat of the "solidified solution" is always *greater* than that deducible from the specific heats of the constituents in the solid and gaseous states respectively.

From the great differences in the specific heat of the occluded hydrogen calculated as above, it is evident that charged palladium cannot be regarded as a mixture of a definite palladium hydride, Pd_mH_n, and excess of palladium, for in that case either a constant value would be found, or the alteration in specific heat of the hydrogen calculated as above would be proportionate to the quantity of hydrogen, which is not the case, the mean curve being actually a curve and not a straight line.

If, therefore, palladium charged to various extents with hydrogen be neither mixtures of palladium and hydrogen, nor of palladium hydride and palladium, it will follow that each several charge must be regarded as giving rise to a distinct compound, and therefore that palladium and hydrogen, like hydrogen chloride and water, are capable of entering into combination in proportions which are *not* expressible by taking and comparing simple multiples of the combining numbers of these elements respectively, *i.e.*, in proportions which are *not* expressible by simple formulæ.

VIII.—*On the Standardising of Acids.*

By Walter Noel Hartley, F.C.S., King's College, London.

Desiring on one occasion to standardize a nearly normal solution of sulphuric acid in a short space of time, the following method occurred to me, which is so convenient that I have ever since employed it.

A block of sodium is cleansed from naphtha by pressure between folds of filter-paper, and cut rapidly with a large cork-knife, so that each surface is but very little tarnished, giving the metal a purplish or bluish tint. The piece of metal, which of course must not be touched with the fingers, is instantly placed in a capsule, such as may be made out of two test-tubes by cutting off their lips and inverting one within the other. When the tubes fit properly, sodium can be weighed in them as accurately as can be wished. The sodium is dissolved in 50

to 100 c.c. of pure alcohol, in a flask of 350 c.c. capacity, the neck of which is inclined, a stream of water running over the body of the flask to cool it. When the sodium ethylate becomes viscid and the action slow, a drop of water may be added, and this effects quietly and completely the solution of the metal. If a deci-normal solution of alkali is desired, it is only necessary to make up the liquid to the required volume. If, however, a simple titration to fix the strength of an acid is wanted, dilute with an equal bulk or more of water, and proceed as usual.

That the method is a good one is evidenced by the fact that students obtain better results with it than by titrating with sodium carbonate, because the solution is almost entirely caustic, which saves them much of the trouble caused by the liberation of a large quantity of carbonic acid in the ordinary way. The first attempt at quantitative work, made by Mr. Duncan, a student in this laboratory, gave the following results:—

	Weight of sodium.		Acid c.c.		H_2SO_4 in 1000.
(1)	0·620	required	25·8	=	51·20
(2)	0·713	„	29·7	=	51·13
(3)	0·742	„	30·7	=	51·42
			Mean	=	51·25

The pieces of sodium were weighed in a capsule and dropped one after the other into flasks containing alcohol, the weight of each piece of sodium being of course known by difference.

Two precipitations with barium chloride of 25 c.c. of the acid gave in each case 3·041 grams $BaSO_4$, indicating 51·2 parts H_2SO_4 per 1,000. Titration with sodium carbonate gave 51·8 — 51·4 and 50·4 parts H_2SO_4 in 1,000. I have prepared caustic soda, when wanting a little quite pure as a reagent, by commencing the solution as above in alcohol until the action was sluggish, then adding a little water and a little sodium, keeping the liquid thick, finally adding more water, and evaporating down.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Direct Visibility of the Ultra-violet Rays. By M. SEKULIC (Pogg. Ann., cxlvi, 157).

BY viewing the direct solar spectrum through a spectroscope with two flint glass prisms, and adjusting the collimator so that the sun's image was projected on the refracting surface of the prism, the author was able to see the light of the spectrum and the dark lines as far as the N-group. The colour of the light was light-blue, or almost silver-grey, without a trace of red. On interposing a blue glass, the field of the telescope appeared to be filled with a light-blue mist, like the fluorescent light of quinine, with the dark lines in the back drawn, as it were, on a silver band. With a violet glass, the nebulous light disappears entirely, and the silver band is much more distinctly seen, with all the lines on a perfectly dark field. The lines thus seen were found to agree exactly in position with those which Muller has determined by comparison of photographic spectra (see his *Lehrbuch der Physik*).

H. W.

Bunsen's Chromic Acid Battery. By JOH. MÜLLER (Dingl. Polyt. J., ccv, 104—109).

THE electromotive force, e, and the internal resistance, ω, of a Bunsen's chromic acid battery were found to be—

	e.	ω.
At the commencement	21	0·33
After 45 minutes	21·3	0·53
„ 90 „	9·7	2·19

The electromotive force had not diminished during the first 45 minutes, whilst the resistance had increased. After 90 minutes the electromotive force had sunk to less than one half, whilst the resistance had become nearly seven times as great as at first. Although the battery gives highly satisfactory results for a certain length of time, it follows from the above numbers that it cannot be employed with advantage when the current has sunk below one-third of its original strength, as then the electromotive force diminishes as rapidly as the resistance increases. When the same zinc and carbon, which in the chromate solution had given an electromotive force of 21, were immersed in dilute sulphuric acid, where the galvanic polarisation was not prevented, the electromotive force was only 2·8.

R. S.

On the Affinity of Hydrogen for the Non-metallic Elements. By JULIUS THOMSEN (Deut. Chem. Ges. Ber., v, 769—776).

As the heats of combination of hydrogen with the non-metallic elements are involved in many thermo-chemical calculations, the author has thought it important to re-determine them.

1. *Chlorine.*—The reaction (H,Cl) = 22001 heat-units was determined by direct combustion of chlorine in dry hydrogen. (HCl,Aq), or the absorption of gaseous hydrogen chloride by water was found to furnish 17314 heat-units, from which follows (H,Cl,Aq) = 39315 heat-units.

2. *Bromine.*—On decomposing an aqueous solution of potassium bromide by chlorine, the liberated bromine then remaining in solution, it was found that KBrAq,Cl = 11478 heat-units. From this and from the previously determined reactions (Br,Aq) = 539 heat-units, (H,Cl,Aq) = 39315 heat-units, (KHO,HClAq) = 13740 heat-units, and (KHOAq,HBrAq) = 13750 heat-units, we derive (BrAq,H) = 27837 heat-units, and (Br,H,Aq) = 28376 heat-units. As the absorption of hydrogen bromide by water or (HBr,Aq) gives 19207 heat-units, we obtain finally 8440 heat-units as expressing the affinity of bromine for hydrogen.

3. *Iodine.*—The experimental results (KIAq,Cl) = 26209 heat-units, (HKOAq,HIAq) = 13675 heat-units, (HI,Aq) = 19207 heat-units, give by calculation (H,I,Aq) = 13171 heat-units, and (I,H) = −6036 heat-units.

4. *Oxygen.*—Direct experiment gave (H_2,O) = 68357 heat-units.

5. *Sulphur.*—The heat was estimated which is evolved on passing gaseous hydrogen sulphide into a solution of iodine in dilute hydriodic acid, in which iodine dissolves more freely than in pure water and without change of temperature. The experimental results (I_2,Aq,SH_2) = 21830 heat-units, and (I,H,Aq) = 13171 heat-units, furnish (H_2,S) = 4512 heat-units, and, as (H_2S,Aq) is = 4754 heat-units, the total heat of combination of hydrogen sulphide dissolved in water is expressed by (H_2,S,Aq) = 9266 heat-units.

6. *Nitrogen.*—Every atom of chlorine passed into an aqueous solution of ammonia produces 39871 heat-units, or ($n$$NH_3$Aq,Cl) = 39871 heat-units, and as besides (HCl,Aq,NH_3Aq) = 12270 heat-units, we obtain for the affinity between hydrogen and nitrogen in an aqueous ammonia solution—

(N,H_3,Aq)	=	35142	heat-units.
But (NH_3,Aq)	=	8435	„ ; therefore
(N,H_3)	=	26707	„

The mode of calculating the total heat of combination of the ammonium compounds is indicated by the equation—

$$(NH_4,Cl,Aq) = (N,H_3,Aq) + (H.Cl,Aq) + (NH_3Aq,HClAq).$$

From his former determinations of the reactions on the right-hand side the author obtains—

(N,H_4,Cl,Aq)	=	86730	heat-units.
(N,H_4,Br,Aq)	=	75790	„
(N,H_4,I,Aq)	=	60580	„
(N,H_5,S,Aq)	=	50600	„

As also the latent heats of solution of the first three of these compounds are known—

$$(NH_4Cl,Aq) = -\ 3880 \text{ heat-units.}$$
$$(NH_4Br,Aq) = -\ 4380 \quad ,,$$
$$(NH_4I,Aq) = -\ 3550 \quad ,,$$

the heats of combination of the ammonium compounds in the solid state can be calculated—

$$(N,H_4,Cl,) = 90610 \text{ heat-units.}$$
$$(N,H_4,Br) = 80170 \quad ,,$$
$$(N,H_4,I) = 64130 \quad ,,$$

7. *Carbon.*—The author has not only redetermined the heats of combustion of ethylene, but also estimated that of acetylene.

Marsh-gas.—As the heats of combustion of marsh-gas, as found by Dulong, Andrews, Favre, and Silbermann do not differ much from each other, the author adopts the mean of these determinations—

$$CH_4,O_4 = 20900 \text{ heat-units,}$$

from which the affinity of hydrogen and carbon follows by the equation—

$$(CH_4,O_4) = 209900 \text{ heat-units} = (C,O_2) + 2(H_2,O) - (C,H_4).$$

If for (C,O_2) we introduce the number found for the heat of combustion of graphite, then

$$(C,H_4) = 20420 \text{ heat-units.}$$

The affinity of carbon and hydrogen in marsh gas is therefore positive.

Ethylene.—The heat of combustion of this gas is, according to the author's experiments—

$$(C_2H_4,O_6) = 334800 \text{ heat-units,}$$

from which, by the equation—

$$(C_2H_4,O_6) = 2(C,O_2) + 2(H_2,O) - (C_2,H_4),$$

follows—

$$(C_2,H_4) = -\ 10880 \text{ heat-units.}$$

Acetylene.—The affinity of carbon and hydrogen in acetylene is calculated from its heat of combustion—

$$(C_2H_2,O_5) = 310570 \text{ heat-units,}$$

from which, by the equation—

$$(C_2H_2,O_5) = 2(C,O_2) + (H_2,O) - (C_2,H_2),$$

follows

$$(C_2,H_2) = -\ 55010 \text{ heat-units.}$$

The affinity of hydrogen for every first member of the four natural groups of the non-metallic elements is positive, but diminishes for the members with greater atomic weights, and is even negative for some of

the highest members. Although no satisfactory explanation of this can be given at present, it must, at all events, be remembered that many thermo-chemical equations do not represent the actual physical conditions, inasmuch as they express the reactions of atoms upon each other instead of molecules. Thus the heat of combustion of hydrogen in chlorine ought to be expressed, not by ClH = 22001 heat-units, but by $(Cl_2,H_2) = 44002$ heat-units, and the true value of the (Cl,H) can only be calculated from the equation $(Cl_2,H_2) = 2(Cl,H) - (Cl,Cl) - (H,H)$, in which the terms on the right hand side are at present unknown.

From the reactions—

$$(C_2,H_2) = -\ 55010 \text{ heat-units.}$$
$$(C_2,H_4) = -\ 10880 \quad ,,$$
$$(C,H_4) = +\ 20420 \quad ,,$$

it might appear that the affinity of carbon for hydrogen is negative. but as the hydrocarbons once formed produce a great amount of heat in their combination with more hydrogen, and are remarkable for their stability, it can scarcely be doubted that the affinity of carbon for hydrogen is really positive.

The fact that the formation of the lower compounds of carbon with hydrogen and oxygen produces less heat than their combination with more hydrogen or oxygen, and that the direct combination of carbon with other elements can only be effected at very high temperatures, can perhaps be explained by the following hypothesis:—

The carbon, as it is known as graphite, diamond, or charcoal, is in a negative or passive condition, out of which it must be brought before it can chemically combine with other elements, a certain amount of force being necessary to effect this transformation from the passive into the chemically active state.

This force cannot at present be estimated, but amounts probably to about 70000 heat-units for every carbon atom.

R. S.

Slow Combustion. By P. J. VAN KERCKHOFF (Chem. News, xxvi, 219—221).

THE author's experiments were conducted by passing mixtures of oxygen and carbon monoxide, and also oxygen and ordinary coal gas (purified from carbon dioxide) through U-tubes, containing, (1) platinised asbestos, (2) purified pumice-stone, (3) purified pipe-clay. By passing the resultant gases through lime-water, the formation of carbon dioxide, and therefore the combustion of the gases used, was rendered manifest. Platinized asbestos in every instance brought about the slow combustion of the gases; pipe-clay and pumice did not, unless the contact of the gases under their influence was protracted. The higher the temperature the shorter the time of contact required. Pumice-stone becomes thus active at a lower temperature than pipe-clay, in the case of carbon moxoxide, but the reverse is true when coal-gas is used. The carbon dioxide formed is for the greater part retained by the pipe-clay; also to some extent by pumice-stone; and is expelled only at a higher temperature than that at which it is formed.

M. M. P. M.

Determination of the true Zero of Thermometers.

By C. TELLIER (Chem. News, xxvi, 249).

In the author's opinion the variation in the zero point of sensitive thermometers does not depend so much upon a modification of the glass, as usually admitted, as upon an erroneous determination of the 0°, and satisfactory reasons are advanced in support of this opinion. Of seven thermometers by the best makers, only one was found to indicate 0° correctly, the greatest variation being + 0·4°. The following method for determining the true zero, or, employing the author's phraseology, the "terminus of congelation," will be found to give trustworthy results:—

A glass vessel containing water is placed in a refrigerating mixture, and the temperature of the water lowered to −2° or −3°. The vessel is then removed from the mixture, and the thermometers to be graduated are immersed in the water. On the introduction of a small piece of ice, the water suddenly freezes, and at the same time the temperature rises to 0°. When no ice is at hand, the temperature of the water should be brought down to −4°, when, by giving a gentle tap with a glass rod to the bottom of the vessel, congelation of the water will ensue, and the temperature rise to the true 0° absolutely.

J. W.

Regulation of Gas Flames for Temperatures above the Boiling-point of Mercury.

By G. MYERS (Deut. Chem. Ges. Ber., v., 859).

The author refers to a modification of Schlösing's regulator, in which, instead of the mercury reservoir, a reservoir of air consisting of four tubes, each 15 cm. long and 2 cm. wide, placed side by side, is employed. The variation with the modified instrument does not exceed 5°. It cannot be employed, however, in its present form for temperatures above the boiling point of mercury; and the same objection applies, according to the author, to the recently described regulators of Jeannel and Martenson (*Chem. Centralbl.*, 1872, 460 and 497).

H. E. A.

Researches on Crystalline Dissociation. A New Method of Studying the Coercive Action of Salts on Water at Different Temperatures.

By P. A. FAVRE and C. A. VALSON (Compt. rend., lxxv, 1066, 1071).

The authors have hitherto studied the coercive action of salts on water, by means of the determination of the densities of the saline solutions; but as this method does not allow of observing the progress of the action, or the modifications corresponding to the changes of temperature, they have devised a special apparatus for this purpose. It consists of a glass vessel of known capacity, having at its upper extremity two tubulures furnished with metallic screw caps. Through one of these passes the stem of a thermometer, and in the other—which is furnished with a lateral stopcock—is inserted a narrow tube, graduated in fractions of the capacity of the reservoir. The vessel being com-

pletely filled with the saline solution, the stopcock is closed, and a column of pure water introduced into the graduated tube, to prevent crystallisation there, the two liquids being imperfectly separated by a glass bulb, which acts as a sort of valve.

This apparatus is useful, not only for determining the co-efficient of contraction of liquids and saline solutions, but also of solid bodies, by introducing them into the apparatus containing a liquid which has no action on them, and whose co-efficient is already known. It will be especially useful in analysing the phenomenon of contraction which takes place in water under the influence of the salt it holds in solution. The authors have employed it in observing the changes which take place during the separation of anhydrous sodium sulphate, when the temperature of a solution of that salt saturated at 32·7° is raised; they have also observed the effects produced on lowering the temperature of a similar solution, and find that when no separation of crystals occurred, the solution remaining supersaturated, the contraction was considerably less than when crystallisation was induced by the introduction of a minute crystal into the liquid through the calibrated tube. In the latter case the temperature of the solution rose from 21·40° to 29·85°, and it was found that a much longer time was required for it to return to the normal temperature than for a supersaturated solution owing to the crystals being bad conductors of heat. From this it would seem that the supersaturated solution, and the solution of the salt which has deposited the crystals, are in very different coercive states, the potential force stored up as it were in the supersaturated solution presenting a striking analogy with that in explosive substances.

C. E. G.

The Structure of Isomorphous Crystals. By H. BAUMHAUER (Deut. Chem. Ges. Ber., v, 857—859).

THE author refers to Rammelsberg's view (*Deut. Chem. Ges. Ber.*, ii, 31) that the molecule of a crystal consists of a group of single molecules, and to the discussion (*ibid.* ii, 652) of the isomorphism of certain ferrous salts with magnesium or calcium salts by Kekulé, who was led to infer that a like crystalline form does not necessarily imply a similarity of the molecules on all sides, but may be a consequence of partial similarity, and perhaps even of similarity on one side only of the molecules.

Certain observations made by the author on the form of the corrosion-figures produced by the action of solvents on various isomorphous crystals appear to him to favour this latter view. These corrosion figures are mostly microscopic hollows bounded by regular surfaces, the form of which evidently bears a certain relation to the general proportions of symmetry of the crystal. The figures produced on isomorphous crystals always exhibit a certain similarity of form, but have not always the same position relative to the surfaces of the crystal. Thus there is no important difference between the figures produced by water with the isomorphous members of the monoclinic group, sulphate of iron, sulphate of iron and ammonium, sulphate of nickel and potassium, and sulphate of nickel and ammonium. The figures correspond in position,

although the analogous surfaces of these bodies do not behave in exactly the same manner (which is in accordance with the slight differences of angle existing between them). In particular the figures on the two latter salts resemble each other very closely.

The group calcspar, dolomite, and spathic iron ore exhibits a contrary behaviour. Hydrochloric acid produces on the rhombohedral cleavage-planes of calcspar hollows of the form of an isocoles triangle, with the apex towards the terminal summit of the crystal. Similar figures are produced by hydrochloric acid on the rhombohedral cleavage-planes of spathic iron ore, but in this case the base of the triangular hollow is towards the terminal summit of the crystal. According to Haushofer dolomite behaves similarly to spathic iron ore.

The close resemblance or difference in the position of the corrosion-figures in these isomorphous bodies would appear to point to a resemblance or difference in the structure or molecular form of the crystals.

H. E. A.

New Application of Tube Hydrometers. By WILSON H. PILE (Chem. News, xxvi, 248).

A PLAIN cylindrical tube of thin glass, closed at one end (a tube hydrometer), can be used for determining the specific gravity of liquids, by employing it in the following manner:—The tube is immersed in water, and water poured into it until it floats upright. The surface of the water, both outside and inside the tube is noted, and the tube below the latter mark divided into 145 parts. To ascertain the density of a liquid heavier than water, the tube is immersed in water at 15·5°, and the liquid to be tried poured in until the instrument sinks to the upper mark. The etched divisions upon the glass will then show the density of the liquid, according to Baumé's scale. In order to make a scale for liquids lighter than water, the space below the surface of the water in the tube must be divided into 140 parts, since Baumé's degrees for light liquids differ from those employed for heavy liquids; the degrees are then continued upwards for about 70 parts. These divisions are numbered upwards, calling the water-point 10° (another peculiarity of Baumé's scale). The tube when constructed is made use of, as in the previous instance.

The principal advantage claimed for these hydrometers by the author is, that they can be used with exceedingly small quantities of liquid.

J. W.

A New Water Air-Pump. By C. CHRISTIANSEN (Pogg. Ann. cxlvi, 155).

THIS is a modification of the well-known aspirator of Johnson. A thick-sided caoutchouc tube attached to a water-tap, is pierced a little below with a red-hot needle, and into the aperture thus made is inserted the shorter arm of a glass tube, bent at right angles, the aperture being directed downwards. On setting the water running, only a slight suction is perceived until the caoutchouc tube is pinched a little below the end of the glass tube. The point at which the pressure must be

made in order to produce the most rapid exhaustion must be found by trial. When the apparatus acts well, the pressure in a vessel connected with the glass tube may be reduced very nearly to the tension of water-vapour at the temperature existing in the vessel.

H. W.

Application of the Water Air-Pump to Evaporation, Distillation, Filtration, &c., in vacuo. By F. A. WOLFF (Dingl. Polyt., J., ccv, 305—310).

An Improved Form of Filter-Pump. By T. E. THORPE (Phil. Mag. [4], xliv, 249).

Convenient Gas-Generators. By V. WARTHA (Dingl. Polyt. J., ccv, 203).

Observations on the Mercury Calorimeter. By M. BERTHELOT (Bull. Soc. Chim. [2], xviii, 57, 388).

Observations on the Criticisms which have been made respecting the Mercury Calorimeter. By P. A. FAVRE (Ann. Chim. Phys. [4], xxvi, 384; Bull. Soc. Chim. [2], xviii, 385).

On the Nature of the Elements. By J. GROSHANS (Deut. Chem. Ges. Ber., v, 689, 754).

Inorganic Chemistry.

Preparation of Pure Hydrochloric Acid. By HERMANN HAGER; also by TH. DIEZ (Chem. Centr., 1872, 418).

HAGER does not consider the method of Bettendorf trustworthy, and suggests a plan which consists in diluting the acid to 1·13 sp. gr., digesting at 30° with copper, and subsequently distilling.

Diez suggests saturating the acid of 1·13 sp. gr. with sulphuretted hydrogen, allowing the arsenious sulphide to subside, then distilling the liquid as long as the distillate smells of the gas.

A. T.

Existence and Dissociation of Sulphur Tetrachloride. By A. MICHAELIS and O. SCHIFFERDECKER (Deut. Chem. Ges. Ber., v, 924—928).

CARIUS considered sulphur tetrachloride to exist in the chloride saturated with chlorine, principally because by treating it with benzoic acid

and alcohol he had obtained evidence that thionyl chloride was formed, though not of course in the free state. By acting upon sulphuric anhydride with sulphur chloride and chlorine, the authors have succeeded in establishing beyond dispute this formation of thionyl chloride, so much so, indeed, that this reaction actually furnishes an advantageous method of preparing this body.

The sulphuric anhydride is distilled from its solution in sulphuric acid into the sulphur dichloride in a current of chlorine. Towards the end of the experiment a little sulphurous anhydride is developed. The excess of chlorine is removed by a current of carbon dioxide and the product is distilled. There are thus obtained thionyl chloride and $S_2O_5Cl_2$.

The thionyl chloride being derived from sulphur tetrachloride, the reaction will be represented by the equation—

$$SCl_4 + S_2O_6 = SOCl_2 + S_2O_5Cl_2,$$

and the small quantity of sulphurous anhydride that is formed may be attributed to the action of sulphuric anhydride upon the thionyl chloride formed. If the thionyl chloride be derived from sulphur dichloride by its direct oxidation, the reaction will be represented by the equation—

$$4SO_3 + 2SCl_2 = S_2O_5Cl_2 + SOCl_2 + 3SO_2,$$

that is

$$SCl_2 + SO_3 = SOCl_2 + SO_2,$$

and

$$SOCl_2 + S_2O_6 = S_2O_5Cl_2 + SO_2.$$

The authors have in fact ascertained that when $SOCl_2$ and S_2O_6 react, nearly the calculated quantity of $S_2O_5Cl_2$ and much SO_2 are produced. But that the thionyl chloride is formed from the tetrachloride, and not from the dichloride of sulphur in the process they adopt, is proved by the fact that the amount of it obtained is much in excess of that calculated from the second equation, and approaches that indicated by the first; also by the smallness of the quantity of sulphurous anhydride produced.

When twice the quantity of the sulphur chloride is employed, the reaction takes place according to the equation—

$$SCl_4 + SO_3 = SOCl_2 + SO_2 + Cl_2,$$

the chloride SO_2Cl_2 being broken up into its components, just as occurs when PCl_5 is employed.

These results prove that SCl_4 actually exists, but in a dissociated condition, even at $-19°$, so that its molecule consists partly of SCl_4 and partly of SCl_2 and Cl_2. Its action is analogous to that of phosphorus perchloride—

$$\begin{aligned} PCl_5 + S_2O_6 &= PCl_3O + S_2O_5Cl_2. \\ PCl_5 + SO_3 &= PCl_3O + SO_2 + Cl_2. \\ SCl_4 + S_2O_6 &= SCl_2O + S_2O_5Cl_2. \\ SCl_4 + SO_3 &= SCl_2O + SO_2 + Cl_2. \end{aligned}$$

Just as phosphorus perchloride at higher temperatures splits up into chlorine and PCl_3, so that in a stream of gas only PCl_3 remains, so sulphur perchloride splits up into SCl_2 and Cl_2, only that in this case the decomposition takes place at a much lower temperature. Herein lies the explanation of the fact observed by Hubner and Guerout, that sulphur chloride saturated with chlorine is resolved by a current of carbon dioxide into SCl_2 and chlorine.

Hence it appears that two chlorides of sulphur, as of phosphorus, exist, SCl_2 and SCl_4, from which are derived—

$$\begin{array}{ll} SCl_2O & PCl_3O \\ SCl_2S & PCl_3S, \end{array}$$

the compound S_2Cl_2 being not a chloride but a sulpho-chloride of sulphur.

At ordinary temperatures sulphur chloride and SO_3HCl react in a stream of chlorine like SCl_4 and SO_3, as regards two-thirds of the chloride; the remaining third behaves like SCl_2. But when cooled down, a crystalline body is obtained which appears to be Millon's $S_2O_3Cl_4$, the rational formula of which may be $SO_2Cl—O—SCl_3$.

Michaelis inserts in a foot note particulars communicated to him by Prof. Geuther of the action of PCl_5 upon $S_2O_5Cl_2$, and of PCl_3 upon SO_4H_2. He himself had found that, when warmed together, PCl_5 and $S_2O_5H_2$ yielded PCl_3O and $SO_2 + Cl_2$, instead of SO_2Cl_2, and that in the cold they had no marked action upon each other. Geuther sealed them up and exposed them to sunshine for two years and a half, and obtained $SOCl_2$, $POCl_3$, and chlorine—

$$\begin{array}{l} S_2O_5Cl_2 + PCl_5 = 2SO_2 + 2Cl_2 + PCl_3O \\ PCl_5 + SO_2 = PCl_3O + SCl_2O, \end{array}$$

so that in this case also, instead of SO_2Cl_2, only its components were obtained.

The action of PCl_3 upon SO_4H_2 is represented by the equation—

$$2SO_4H_2 + PCl_3 = SO_3HCl + SO_2 + PO_3H + 2ClH.$$

E. D.

On Barbaglia and Kekulé's Explanation of the Action of Phosphoric Chloride on Sulpho-chlorides. By A. MICHAELIS (Deut. Chem. Ges. Ber., v, 929).

BARBAGLIA and Kekulé have shown that benzenesulphonic chloride is decomposed by PCl_5 at 200°, according to the equation—

$$C_6H_5.SO_2Cl + PCl_5 = C_6H_5Cl + SOCl_2 + POCl_3.$$

They assume that in the first place $PSCl_3$ is formed, which is then converted by the yet unknown oxide of chlorine, Cl_2O_2, simultaneously produced into $SOCl_2$ and $POCl_3$

The author believes the reaction admits of a simpler interpretation, represented by the equations—

$$\begin{array}{l} C_6H_5.SO_2Cl + Cl_2 = C_6H_5Cl + SO_2Cl_2, \\ SO_2Cl_2 + PCl_3 = SOCl_2 + POCl_3. \end{array}$$

Composition of Ammonium Amalgam. By R. ROUTLEDGE (Chem. News, xxvi, 210—212).

THE author has endeavoured to determine—

(1.) Whether by the decomposition of this amalgam, ammonia and hydrogen are evolved in atomic proportions. To this his experiments answer yes.

(2.) Whether the ammonium which, he concludes, is present in the amalgam, exists as a gas or chemically combined with metallic mercury. To this his experiments answer most probably combined. He supposes, and this seems to be supported by his experiments, that a compound of ammonium and mercury is formed, but that this immediately begins to decompose, and that the ammonia and hydrogen thus set free get entangled in the mercury, and so cause it to swell and froth up.

M. M. P. M.

Preparation of Pure Potassium Bromide. By FALIÈRES (Chem Centr., 1872, 419).

To remove iodine, add excess of bromine water, and boil. Bromine may be freed from chlorine by the addition of potassium bromide. Pure potassium bicarbonate may be used in the preparation instead of impure potassium hydrate.

A. T.

Action of Silica and analogous Oxides upon Sodium Carbonate. By M. MALLARD (Compt. rend., lxxv, 472—474).

WHEN silicic acid and sodium carbonate are heated together in a platinum crucible, the loss of carbonic acid is found to tend to a certain limit, different for different temperatures. The rate at which the loss increases with the time can be expressed by the equation—

$$y = \frac{ax}{b + x},$$

where y = loss of carbonic acid, x = time.

In order to explain why the result varies with the temperature, the author assumes that at the commencement of the reaction an acid silicate is formed, which decomposes again into neutral silicate and silicic acid, which acts upon more sodium carbonate until a state of equilibrium is attained between the neutral and acid silicates and the silicic acid. This equilibrium is of course dependent upon the temperature. A similar explanation applies probably to the reaction of the bibasic compounds, titanic acid and zirconia, upon sodium carbonate.

Alumina and ferric oxide, on the other hand, and boric acid behave as monobasic acids; when melted with sodium carbonate they form immediately or in a few minutes, the compounds $Al_2O_3.Na_2O$, $Fe_2O_3.Na_2O$, and $Bo_2O_3.3Na_2O$, and the result is not modified by elevation of temperature.

R. S.

Magnesium Oxychloride. By O. Krause (Ann. Chem. Pharm., clxv, 38—44).

Bender (*Ann. Chem. Pharm.*, clix, 341) prepared a paste by mixing magnesia with solution of magnesium chloride, exposed it to the air during six months, and then analysed it. The carbonic acid present was calculated as anhydrous magnesium carbonate; this was subtracted, and the residue was found to correspond approximately with the formula $MgCl_2.5MgO + 17H_2O$. But as magnesium hydrate is not entirely converted into carbonate by exposure to the air, the author concludes that Bender's results do not express the true composition of magnesium oxychloride.

In order to determine this point, freshly ignited magnesia was treated with a large excess of magnesium chloride solution, the whole being heated in a water-bath, and continually agitated. When a microscopical examination showed that the solid portion of the mixture consisted entirely of needle-shaped crystals, the whole was thrown on a filter and washed with water.

The needles thus obtained, when dried at 110°, were found to consist of $MgCl_2.10MgO + 14H_2O$, and, when dried over sodium hydrate, they were found to contain $MgCl_2.10MgO + 18H_2O$.

The crystals of this magnesium oxychloride were destroyed when moist, by the action of carbonic anhydride. When, however, the dry crystals were exposed to the action of this gas, no change was observed.

These experiments show that the hydraulic mass formed by kneading magnesia with a solution of magnesium chloride, consists of basic magnesium carbonate and crystals of the compound $MgCl_2.10MgO + 18H_2O$.

T. B.

The Combinations of Yttrium and of Erbium. By P. T. Clève and O. Hœglund (Bull. Soc. Chim. de Paris), 193—201, and 289—297).

In an introductory sketch of the history of the metals yttrium, erbium, terbium, &c., the authors lay before the reader a concise but interesting account of the investigations of earlier chemists respecting these metals. The chemistry of these elements as it exists at the present day, may be very briefly summarized.

The existence of yttrium and erbium is undoubted, but the elementary nature of terbium has never been either satisfactorily ascertained or disproved. It is doubtful whether the combinations of yttrium and erbium have ever been obtained in a state of purity, and the determinations of their atomic weights have varied so greatly, that no reliance whatever can be placed upon them. The authors have therefore undertaken a new series of researches upon the earthy oxides contained in gadolinite, in order to determine, firstly, whether the mineral contains two or three distinct oxides, and secondly, to study some of the combinations and distinctive characteristics of these oxides, so as to be able to originate a new and more accurate method of separation. They

have searched in vain for the third earth (the *erbia* of Delafontaine, or *terbia* of Mosander); they obtained only mixtures of erbium, yttrium, and didymium. The salts of the two former metals were prepared and separated, and their atomic weights determined by the method originally proposed by Bahr and Bunsen.

An attempt to prepare the metals by electrolysing the fused chlorides, or by reducing the chlorides by sodium, was only partially successful.

YTTRIUM SALTS.—*Atomic Weight.*—A mean of five determinations gave the number 59·7 as the atomic weight of yttrium; an oxide of great purity being operated upon. The salts of yttrium are colourless; their solutions do *not* give an absorption spectrum, and they are, as a rule, less soluble than the corresponding salts of erbium. Both yttrium and erbium salts are precipitated by barium carbonate, a result contrary to the experience of some experimenters. The *hydrate of yttrium* is a white, gelatinous precipitate, obtained by the addition of a fixed alkali to a salt of yttrium. When calcined at a white heat it is converted into *yttrium oxide*, a yellowish-white powder, very readily soluble in acids, even after ignition.

For a description of the preparation, and for the details of the analyses of the following salts, we must refer the reader to the original paper.

Yttrium Chloride, $YCl_2 + 4H_2O$, forms deliquescent prisms, soluble in alcohol, insoluble in ether. When heated it loses hydrochloric acid, but the anhydrous chloride can be prepared by fusing together a mixture of hydrated chloride and sal-ammoniac.

Yttrium Bromide, $YBr_2 + 6H_2O$, and *yttrium iodide* closely resemble the chloride in appearance and solubility. The iodide is unstable, and becomes brown rapidly when exposed to the air. It does not appear to have been analysed.

Yttrium Fluoride, YFl_2, is a heavy, white, hygroscopic powder, but slightly soluble in dilute acids.

Yttrium Nitrate, $Y(NO_3)_2 + 4H_2O$, occurs in large, colourless crystals, easily soluble in water, alcohol, and ether. It is unalterable in the air, but loses two molecules of water when dried at 100°.

Yttrium Chlorate, $Y(ClO_3)_2 + 6H_2O$.—The crystals of this salt are small, colourless prisms, exceedingly deliquescent; soluble in alcohol, but very slightly so in ether.

Yttrium Perchlorate, $Y(ClO_4) + 6H_2O$ (?).—Transparent crystals, very deliquescent, slightly soluble in alcohol.

Yttrium Bromate, $Y(BrO_3)_2 + 6H_2O$.—Colourless needles, very soluble in water, slightly soluble in alcohol, almost insoluble in ether. It decomposes at 100°—110°. The *iodate* is a very definite salt, but not crystalline.

Yttrium Periodate.—Two periodates are capable of being formed, according as the periodic acid employed in their preparation is in excess or not. The salt marked (*a*) is the most definite:

$$(a.)\ Y_8I_6O_{29} + 24H_2O. \qquad (b.)\ Y_9I_4O_{23} + 6H_2O\ (?).$$

Yttrium Sulphate, $3YSO_4 + 8H_2O$.—Small transparent crystals, which lose their water of crystallisation at 115°. 100 parts of water at 15·5° dissolve 9·3 parts of crystallised, and 15·2 parts of anhydrous

sulphate; but on raising the temperature of the latter solution, a portion of the crystallised salt is deposited.

Yttrium Sulphocyanate, $Y(CNS)_3 + 6H_2O$.—Well defined prisms, soluble in water, alcohol, and ether, and permanent in the air.

Yttrium Platinocyanide, $Y(CN)_4Pt + 7H_2O$.—Like many platino-cyanides, this salt crystallises in large, well-defined, dichroic crystals, red by transmitted light, and green or violet blue by reflected light. It is easily soluble in water, but alcohol deprives it of a portion of its water of crystallisation, and changes its colour to a lemon-yellow.

Yttrium and Potassium Ferrocyanide.—$\left.\begin{matrix}K_3\\Y_3\end{matrix}\right\} 12CN.Fe''_2 + 4H_2O$.

Yttrium Cobalticyanide.—$Y_3Co_3Cy_{12} + 5H_2O$ (?).

Yttrium Double Sulphates.—Two potassium salts were obtained, to which the formulæ, $Y_2K_6 5SO_4$ and $Y_2K_2.3SO_4$ were assigned, but the analytical results did not agree very accurately with the calculated percentage. The sodium and ammonium salts were much more definite, and the formulæ, $Y_3Na_2(SO_4)_3 + 2H_2O$, and $Y_3(NH_4)_4(SO_4)_5 + 9H_2O$ may be considered to represent correctly their composition.

Yttrium Sulphite, $YSO_3 + H_2O$ is also a definite salt, crystallising in microscopic needles. It absorbs oxygen rapidly from the air.

Yttrium Seleniate, $YSeO_4 + 3H_2O$ (?) forms large well developed crystals, very soluble, and losing a portion of water of crystallisation in dry air.

Yttrium Selenite, $Y_3H_2(SeO_3)_4$.—This salt occurs either as a white crystalline powder, or in the form of flattened microscopic prisms, according to the manner in which it has been prepared. It is soluble in mineral acids.

Yttrium Phosphates.—The *metaphosphate*, $Y(PO_3)_3$ is a heavy crystalline powder, insoluble in water and acids. The *pyrophosphate*, $Y_3H_3.2P_2O_7 + 7H_2O$, and *orthophosphate*, $Y_3(PO_4)_2 + 4H_2O$ were also prepared. The former is a soluble, and the latter a very sparingly soluble salt.

Yttrium Carbonate, $YCO_3 + H_2O$.—A heavy white powder, indistinctly crystalline, and perfectly insoluble in water.

Yttrium Acetate, $2Y(C_2H_3O_2)_2 + 5H_2O$, crystallises from its solutions in colourless rhombohedra, very soluble in warm water, but very sparingly in cold. It is permanent in the air.

Yttrium Oxalate, $YC_2O_4 + H_2O$.—A white crystalline powder, readily soluble in water, acidulated with hydrochloric acid. It dissolves easily in concentrated solutions of potassium oxalate, with formation of double salts, $Y_3K_8(C_2O_4)_7 + 12H_2O$, and $Y_3K_2(C_2O_4)_4 + H_2O$.

Yttrium Double Carbonates.—$Y_3Na_2(CO_3)_4 + 4H_2O$ and $Y_5(NH_4)_4(CO_3)_7 + 3H_2O$.

Yttrium Succinate.—$YC_4H_4O_4 + xH_2O$ (?).

Yttrium Tartrate, $Y_3H_2(C_4H_4O_6)_4 + 6H_2O$.—A white crystalline precipitate, very slightly soluble in water.

Erbium Salts.—*Atomic Weight*.—The atomic weight of erbium, from a mean of four determinations, was fixed at 113·7.

It is useless to reproduce here the preparation, appearance, or physical characters of the erbium salts, since in almost every instance they correspond with those of yttrium. The only well marked distinctive characteristics are the following.

The salts of erbium possess a beautiful rose colour, and their solutions give absorption-bands. The appearance of the spectrum is quite different from that of didymium. Erbium oxide dissolves with great difficulty, even in concentrated acids. A solution of ammonium oxalate dissolves only traces of yttrium oxalate, but erbium oxalate dissolves in it with great readiness, forming a well defined, crystallisable, double salt.

The following salts were prepared and analysed :—

Erbium Salts.

Chloride..................	$ErCl_2 + 4H_2O$.
Bromide	$ErBr_2 + H_2O$.
Sulphocyanate	$Er(CNS)_2 + 4H_2O$.
Chlorate..................	$Er(ClO_3)_2 + 6H_2O$ (?)
Iodate	$Er(IO_3)_2 + 2H_2O$.
Sulphate	$(ErSO_4)_3 + 8H_2O$.
Selenite..................	$Er_3H_2(SeO_3)_4 + 3H_2O$.
Pyrophosphate	$ErH_2(P_2O_7)_2 + 7H_3O$.
Acetate	$Er(C_2H_3O_2)_2 + 3H_2O$.
Succinate	$(ErC_4H_4O_4)_2 + 3H_2O$.
Double potassium sulphate..	$ErK_2(SO_4)_2$.
Double potassium oxalate ..	$Er_4K_8(C_2O_4)_7 + 12H_2O$.
" ammonium "	$Er(NH_4)_6(C_2O_4)_4 + 5H_2O$.
Fluoride	$ErFl_2$.
Ferrocyanide..............	$K_2Er_4Cy_{12}Fe_2 + xH_{20}$.
Nitrate	$Er(NO_3)_2 + 4H_2O$.
Bromate	$Er(BrO_3)_2 + 6H_2O$.
Periodate	$Er_5I_6O_{29} + 2H_2O$.
Sulphite	$ErSO_3 + H_2O$.
Orthophosphate	$Er_3(PO_4)_2 + 2H_2O$.
Carbonate................	$Er_3\left\{\begin{matrix} OH \\ (CO_3)_2 + H_2O \\ OH. \end{matrix}\right.$
Oxalate	$ErC_2O_4 + 2H_2O$.
Platinocyanide............	$Er(CN)_4Pt + 7H_2O$.

Since the greater portion of the salts of yttrium and erbium contain the same quantity of water of crystallisation as the corresponding salts of magnesium and zinc, and since the sulphates are isomorphous with cadmium sulphate, it is probable that these elements might be arranged in the same series as magnesium and its congeners; but it will be noticed that they do not give the double sulphates so characteristic of the magnesian series, $R''R'_2(SO_4)_2 + 6H_2O$. In addition to this, yttrium and erbium enter into numerous combinations with a triple atomic weight, which would seem to imply that they are trivalent elements. The authors having been unable to obtain the metals themselves, and therefore to estimate their specific heat, are unable to decide this question.

No method for the analytical separation of the two bases could be devised.

J. W.

On Ultramarine. By C. Unger (Deut. Chem. Ges. Ber., v, 893—896).

According to an old observation of Berzelius, although ultramarine ignited with soda-lime furnishes only a trace of ammonia, it gives a considerable quantity of free nitrogen gas when fused with phosphorus salt or with an alkaline bisulphate.

The author has examined a sample of ultramarine which contained no sodium sulphide or any sulphur-acid, and after removal of a small quantity of soda and kaolin, he found in 100 parts, 12·6 of sulphur and 5·5 of nitrogen or atomic proportions of the two elements, besides—

14·1 sodium.
14·4 aluminium,
20·4 silicium,
33·0 oxygen.

From the fact that ultramarine treated with acids yields gelatinous silica, the author infers that a silicate is present, and from the results of his analysis he represents the specimen as containing 55·7 per cent. of a silicate of sodium and aluminium in which the oxygen of the acid is to that of the base as 2 : 1, and 44·3 per cent. of the blue body, to which he ascribes the formula $Al_2SiS_2N_2O_3$.

The author next made experiments in order to ascertain whether it was sulphate, sulphite, or hyposulphite, mono- or polysulphide of sodium which on ignition with kaolin gives rise to the production of ultramarine. He found that of these no single salt taken alone was sufficient for the purpose, but that hyposulphite when mixed with sodium carbonate or caustic soda, furnished the blue colour. Further investigation showed that the proportions yielding the most satisfactory results are represented by the following formula:—

$$Al_2O_3 + SiO_2 + 4Na_2S_2O_3 + 2Na_2O, \text{ or } 2Na_2CO_3.$$

As at an early stage of the operation the two sodium salts are decomposed, and half the sulphur is converted into sulphate, and subsequently silicates are formed. It is only a comparatively small proportion of sodium salts which are concerned in the production of ultramarine.

The author represents by the following equations the changes which occur in the production of ultramarine from these materials:—

$$Al_2O_3 + SiO_2 + 4Na_2S_2O_3 + 2Na_2CO_3 = Al_2SO_2 + SiSO + 2Na_2S + 4Na_2SO_4 + 2CO_2.$$

The sodium sulphate and sulphide were removed by washing. During this operation oxygen was absorbed from the air, and on analysis the substance was found to consist of a silicate and the compound $Al_2SiS_2O_5$.

The washed and dried mass, which was coloured slightly bluish-green, gave bright-blue ultramarine on ignition with sal-ammoniac. If heated in sulphur-vapour the mass retained its bluoish-green tint, and assumed the character of ultramarine only when ignited in the

air. In this operation oxygen is removed and nitrogen taken up from the air. In the sample which was the subject of these experiments, there was only about 15 per cent. of the blue body: hence no difference of weight could be observed with certainty, inasmuch as the weight of the nitrogen absorbed is, according to the author's theory, very little less than that of the oxygen which is carried off by the sulphur—

$$Al_2SiS_2O_5 + S = Al_2SiS_2O_3 + SiO_2,$$

and—

$$\underset{\text{Ultramarine.}}{Al_2SiS_2O_3 + N_2 = Al_2SiS_2O_3N_2.}$$

W. A. T.

Action of Chromium Trioxide on Iodine. By I. WALZ (Chem. News, xxvi, 245).

WHEN iodine is placed in a concentrated solution of chromium trioxide, the liquid becomes dark-coloured, and assumes a syrupy consistence. It refuses to crystallise, but may be rendered scaly by spreading on glass plates. When ignited it leaves a residue of green chromium oxide.

There appears to be some indication of the formation of a volatile compound of chromium and iodine, but if so, it is decomposed at a temperature but little above that at which it is formed, and the author failed to isolate it.

If to the solution of chromium trioxide and iodine, sulphuric acid be added, the iodine is rapidly oxidised to iodic acid; the reduction of the chromic acid is, however, under all circumstances, incomplete.

J. W.

Preparation of Platinum Black. By J. LAURENCE SMITH (Chemical News, xxvi, 208).

REDUCE potassium platinum chloride by heating in a platinum crucible over a small Bunsen burner, hydrogen or coal gas being led through a pipe passing through a small circular mica plate which covers the salt in the crucible. Wash the residue with water and dry it.

M. M. P. M.

Mineralogical Chemistry.

Characters of the Crust produced upon Terrestrial Rocks, by Atmospheric Agency, compared with the Black Coating of certain Meteorites. By STANISLAS MEUNIER (Compt. rend., lxxv, 890—893).

THE black incrustation or coating with which grey meteorites are almost invariably clothed, appears to be due principally, if not entirely, to the mechanical action of the air upon the bolide during the passage

of the latter through the earth's atmosphere. This action produces, on the one hand, a sort of varnish or false enamel upon the exterior of the mass, and on the other, a development of heat, which causes the black coloration—the phenomena of fusion, of which, however, indubitable traces may be observed—being only of secondary importance.

This interpretation which was deduced from the direct examination of meteorites, has been strengthened, if not confirmed, by the author's investigation of the phenomena produced by atmospheric agencies upon terrestrial rocks.

His attention was more particularly directed to the subject by the examination of an isolated block of dolerite from Arequipa, Peru. The specimen was invested with a black crust, which might at first sight have been attributed to superficial fusion, had not a microscopical examination and other considerations shown that such an explanation was impossible. The crust was very clearly distinct from the subjacent rock, and was even capable of being detached in the form of thin scales; the natural surfaces of the specimen, therefore, presented a striking resemblance to those of a stone of meteoric origin; at the same time, the peculiarity of the coating and the circumstances under which the stone was found were of such a nature, that the author could not at one time accept without distrust a conclusion which assumed that heat had not in any way participated in its formation.

Any doubts upon the question were however resolved, on the further examination of some blocks of quartzose freestone, found upon the surface of the ground between Villeneuve-Saint-Georges and Limeil (Seine et Oise). These masses, like the previous specimen, closely resembled meteorites, both in their general form and in being covered on all sides with a varnish-like coating, the only sensible difference residing in the fact that the crust was somewhat thicker than is generally found upon meteoric stones, and of an ochreous-red colour (ferric oxide) instead of black.

The investigation, the details of which are given in the original communication, proved not only the intimate analogy existing between the exterior coating of meteorites and that of some terrestrial rock-specimens, but also that they are undoubtedly due to the same cause, namely, mechanical atmospheric agency; only that, in the one case, the friction of the air is very energetic and of short duration, while in the other case, the reverse holds good. J. W.

The Chemical Composition of Humite. By G. vom Rath (Pogg. Ann., cxlvii, 246—263).

Rammelsberg (*ibid.*, lxxxvi, 404—417) from analyses of chondrodite from North America and from Pargas, and of the three types of humite, concluded that these three types and chondrodite are similar compounds of one and the same silicate, $8MgO.3SiO_2$, with varying quantities of a fluoride, $8MgF_2.3SiF_4$, which may be regarded as isomorphous with the silicate; further, that an increase in the proportion of fluorine is accompanied by a shortening of one of the axes of the crystal, the other two remaining the same. To the proportion 2 : 3 : 4 of fluorine atoms in the three types III, I, II, corro-

spond primary forms, in which, with equal bases, the vertical axes are as the numbers $1 : \frac{7}{9} : \frac{5}{9}$ or $9 : 7 : 5$ (see this *Journal*, 1872, p 53).

These results seem to show that the atoms of fluorine possess a power of essentially modifying the crystalline form. v. Kokscharow has, however, shown that chondrodrite—which was referred by Rammelsberg to the same series, but contains the highest proportion of fluorine, and should, therefore, have a primary form still more obtuse than type II—really belongs to that type. If, however, two varieties of humite containing respectively 9 and 5 per cent. of fluorine, can exhibit the same crystalline form, it follows that the morphotropic power supposed to belong to fluorine cannot be exerted in all cases. To throw further light on this point, and determine whether the chemical composition of each of the three types of humite is constant or not, the following investigation was undertaken:—

The chemical analysis of humite is attended with peculiar difficulties, arising partly from the presence of fluorine, but still more from the scarcity of the mineral, and the great care required to separate the crystals of the different types, which often occur together, one from the other, and from the mica with which they are freqently intergrown. The following was the method of analysis adopted:—

A pure specimen of each type having been obtained by very careful selection, with the aid of the microscope, it was finely pulverised, dried at 100°—120°, then fused with four times its weight of dry sodium carbonate, and the fused mass continuously boiled in a platinum dish, first with pure water, then with water containing a little ammonium carbonate. The whole of the sodium fluoride was thereby dissolved, the filtrate moreover containing a large quantity of silica and a not inconsiderable quantity of magnesium fluoride. The filtrate was evaporated, with repeated addition of ammonium carbonate, and the bulky precipitate, after being well washed with hot water, was united with the residue of the fused mass. The filtrate, on further addition of ammonium carbonate, deposited a second quantity of silica, which was united with the first, and the small quantity of silica still remaining in solution was separated, as recommended by H. Rose, by means of a solution of zinc oxide in ammonia, the zinc silicate being afterwards decomposed by nitric acid, the liquid evaporated down, and the small quantity of silica contained in it estimated in the usual way. The fluorine was precipitated from the alkaline solution by calcium chloride; and the precipitate containing calcium fluoride and a large excess of carbonate was dried, ignited, and treated with acetic acid, which dissolved the carbonate (mixed with caustic lime) leaving the fluoride as a gaseous mass. This was dried on the water-bath in a platinum dish, then treated with hot water, collected on a filter, dried, and ignited, whereby the calcium fluoride was obtained as a white powder. The portion of the original fused mass which was insoluble in water, together with the subsequently separated portions of magnesia and silica was treated by known methods for the estimation of silica, magnesia, ferrous oxide, lime, and alumina.

Four specimens were examined, three from Vesuvius and one from Sweden.

Type I, *from Vesuvius.*—Light brownish humite mixed with light green mica, the humite predominating. The mass exhibits cavities (druses), some filled with large thin laminæ of mica, some with pure or nearly pure crystals of humite; some also contain very small quantities of calcspar. Sp. gr. 3·208 (at 15° C.).

Type II. *a. from Vesuvius.*—Light yellow crystalline granules intergrown with light greenish mica, almost silver-white in thin laminæ. A small quantity of admixed calcspar, not mechanically separable, was removed by digestion in acetic acid. Sp. gr. 3·125 (at 13° C.).

Type II. *b. from Sweden.*—Crystals, often very impure in the interior, and consisting, to as much as one-half, of grains of galena, laminæ of green mica, &c. Sp. gr. 3·057.

Type III, *from Vesuvius.*—A block, as large as the first, consisting of predominant humite having an unusual orange-yellow colour, white calcspar, small quantities of greenish and reddish mica, a little white olivine, and isolated slender needles of apatite. Sp. gr. 3·191 (at 17° C.).

Two analyses were made of each type. The numbers given in the following table are the higher of the two values obtained in each case, as the mode of analysis is adapted to give results in defect rather than in excess.

	I.	II*a*.	II*b*.	III.
Silica..........	35·63	34·02	33·96	36·82
Magnesia......	54·45	59·23	53·51	54·92
Ferrous oxide ..	5·12	1·78	6·83	6·48
Lime..........	0·23	—	—	—
Alumina	0·82	0·99	0·72	0·24
Fluorine	2·43	2·74	4·24	2 40
	99·68	98·76	99·26	100·86

Deducting from the several totals the quantities of oxygen corresponding to the fluorine, we find the following losses:—Anal. I = 2·34; II*a* = 2·40; II*b* = 2·52; III = 1·11, whereas an excess might rather have been expected in each case, corresponding to the weight of oxygen replaced by fluorine. These losses appear to be due to water not driven off at 100°—120°, the temperature at which the specimens were dried previous to analysis. The author found that humite dried at 120° gave off 0·34 p. c. water between 120° and 200°.

The following table gives the elementary composition of the several types, after deduction of the oxygen equivalent to the fluorine:—

	I.	II*a*.	II*b*.	III.
Silicon	16·63	15·88	15·85	17·18
Magnesium ..	32·67	35·54	32·11	32·95
Iron	3·98	1·38	5·31	3·07
Calcium	0·16	—	—	—
Aluminium ..	0·44	0 53	0·38	0·13
Fluorine	2·43	2·74	4·24	2·40
Oxygen	41·35	41·54	39·58	43·12
	97·66	97·61	97·47	98·85

If now the iron, calcium, and aluminium be replaced in each case by equivalent quantities of magnesium ($Al_2 = Mg_3$), the quantities of magnesium in the three types of humite become—

I.	IIa.	IIb.	III.
35·04	36·82	34 89	34·43 ;

and dividing these numbers and the quantities of silicon, fluorine, and oxygen by the atomic weights of the respective elements, we find for the relative numbers of atoms of these elements—

	I.	IIa.	IIb.	III.
Silicon	0·594	0·567	0·566	0·613
Magnesium ..	1·460	1·534	1·453	1·435
Fluorine......	0·128	0·144	0 223	0·126
Oxygen	2·584	2·596	2·474	2·695

or, making the number of silicon-atoms = 2, the numbers of the magnesium atoms are—

I.	IIa.	IIb.	III.
5·91	5·41	5·13	4·68

Mean = 5·03.

Hence, neglecting the fluorine, the composition of all humites may be represented by the formula—

$$Mg_5Si_2O_9 \quad \text{or} \quad 5MgO.2SiO_2.$$

This formula, which is simpler than the one formerly given by Rammelsberg, viz., $8MgO.3SiO_2$, may also be deduced from Rammelsberg's own analyses, if they are calculated with the atomic weight of silicon now adopted

The relative numbers of molecules of the silicate and of the fluoride, $Mg_5Si_2F_{18}$, mixed with it are easily calculated from the relative numbers of atoms of the fluorine and oxygen. For 1 atom of fluorine the preceding values give for the numbers of oxygen-atoms—

I.	IIa.	IIb.	III.
20·1	18·0	11·1	21·4

Hence, since each molecule of a fluoride contains twice as many atoms of fluorine as there are atoms of oxygen in the corresponding silicate, it follows that for each molecule of fluoride the numbers of silicate-molecules in the several types are—

40·2 36 22·2 and 42·8 ;

and as the differences of fluorine in the three Vesuvian humites scarcely exceed the ordinary errors of analysis, these three humites may be represented by the same formula, viz. :—

$$40Mg_5Si_2O_9 + Mg_5Si_2F_{18},$$

whereas the Swedish humite contains for the same quantity of fluoride only half that amount of silicate, viz.:—

$$20Mg_5Si_2O_9 + Mg_5Si_2F_{18}.$$

The formula $Mg_5Si_2O_9$ (two-fifths silicate) may be resolved into that of a hemisilicate (or orthosilicate), Mg_2SiO_4, or $2MgO.SiO_2$, and that of a tritosilicate, Mg_3SiO_5, or $3MgO.SiO_2$; and the fluoride, in like manner, may be regarded as a mixture or combination of Mg_2SiF_8 and Mg_3SiF_{10}. The hemisilicate is identical with olivine; the tritosilicate is not known in the separate state. Olivine occurs not unfrequently in very small, nearly colourless crystals, accompanying and intergrown with the humite crystals of Vesuvius.

The general conclusions deducible from the preceding analyses are—(1.) All humites are essentially similar in constitution, and the varying replacement of isomorphous constituents has no decided influence on the types. The variation of colour from the lightest yellow to reddish brown, which is observed in each of the types, shows that the replacement of magnesia by ferrous oxide does not affect the type. Moreover, as the quantities of fluorine in the two varieties of type II are to one another nearly as 1 : 2, a similar variation in the amount of fluorine may be predicted in the other two types. (2.) Humites contain a small, but perhaps never altogether failing quantity of alumina, comparable perhaps with the small quantity of that substance occurring in augitic minerals and in the enstatite of the meteorite of Ibbenbürgen. (3.) The variation in the amount of silica (which appears also from Rammelsberg's analyses) shows that the composition of the several types of humite is not absolutely constant.

No other silicate occurring, in Vesuvius has hitherto been found to contain fluorine. Fluor-spar, which is of extremely rare occurrence in Vesuvian out-casts, has not been found in association with humite.

With regard to the occurrence of humite in Vesuvian out-casts, it may be observed that, whereas some Vesuvian minerals occur chiefly or almost exclusively in blocks of one and the same kind, *e.g.*, mejonite chiefly in limestone blocks, sarcolite exclusively in blocks of green augite, humite is found both in limestone and silicate blocks, the two types of mineral aggregates occurring on Vesuvius. Humites are most frequently associated with mica, light green or reddish-yellow, also with green augite. white olivine, black spinelle (ceilanite), and calcspar; more rarely with vesuvian and garnet; still more rarely with sanidine, mejonite, and nepheline.

Of the three types of humite, I. appears to be the rarest, and III. the most abundant.

H. W.

On some Out-casts of Leucite from Vesuvius. By G. vom Rath (Pogg. Ann., cxlvii, 263—272).

Leucite, the most important and characteristic of all minerals occurring on Vesuvius and in its lavas, is in many respects a remarkable body. and occupies an exceptional place among minerals. It exhibits no varieties, and there are no species isomorphous with it. Of all rock-

forming minerals it is the most limited in the mode of its occurrence. Felspar, which, in a chemical point of view, is most nearly allied to leucite, occurs in rocks of all ages, and in beds of every species, but leucite is never found in veins, very rarely in druses of lava or of ejected masses, never in pseudomorphs. Its occurrence in lava might perhaps seem to remove all doubt as to its mode of formation and its crystallisation from a fused mass. Nevertheless the various minerals which constitute lava cannot all have separated from the mass during solidification. It is possible, and even probable, that leucite may have crystallised from lava, but the crystallisation must have taken place, not during the flow and solidification of the lava on the surface, but in the unknown depths below. On Somma leucite not only forms the lavas, but likewise appears in out-casts, sometimes in limestone blocks, sometimes in sanidine aggregates. The following are descriptions of some remarkable specimens of both these classes of leucitic out-casts.

(*a.*) A lump of limestone about 10 cm. thick, interspersed with grains of calcspar and very small octohedrons of spinelle and periclase, containing moreover numerous roundish cavities from 3 mm. to 3 cm. in diameter, in which occur rounded grains of leucite, some firmly fixed in the cavities, others loose, so that they rattle when the stone is shaken. The leucite in the interior of these grains has the ordinary constitution, and is intergrown with black augite; externally they are covered with a white very prickly crust, consisting of silky, fibrous prisms 1 mm. long, firmly attached to the grains and arranged in nearly parallel rows. This white mineral, when freed by acetic acid from calcium carbonate (amounting to 15—18 p.c. of the whole), gives by analyis 41·1 p.c. silica, 34·5 alumina, 5·6 lime, 0·7 magnesia, and 18·1 loss (alkalis), whence it appears to be d a v y n e.

The calcareous matrix consists of 60·7 p.c. soluble and 39·3 insoluble in acetic acid. The soluble portion is a magnesian limestone containing 86·5 p.c. $CaCO_3$ and 13·5 $MgCO_3$, therefore not a true dolomite. A similar composition was found by Marchand in a fine-grained block of limestone from the Fosso di Pollena.

The insoluble portion of the calcareous matrix appears under the microscope perfectly crystalline, and as a mixture of colourless grains, probably quartz-sand, greenish octohedrons of periclase, black octohedrons of ceilanite, and a very small quantity of magnetic iron ore. It gave by analysis 0·5 p.c. Fe_3O_4, 38·6 SiO_2, 10·7 Al_2O_3, 43·1 MgO, 8·3 FeO (= 101·2). The alumina may be regarded as combined with the magnesia and ferrous oxide, forming ceilanite; the excess of magnesia with the rest of the ferrous oxide forms periclase, while the silica is probably present in the free state. Not a trace of lime was found in the insoluble portion of the matrix.

(*b.*) A stone 12 centimeters thick, having the form of a segment, apparently about one-fourth of the original spheroidal block. It consists of a calcareous shell 3 to 4 cm. thick, surrounding a pear-shaped nucleus of leucite of granular structure and abundantly traversed by black augite. In the interior is a cavity lined with fine crystals of leucite and augite. At the boundary between the shell and the nucleus are numerous shining dodecahedrons of reddish-brown garnet, 1—1½ mm. in size, partly imbedded in the leucite mass, which sepa-

rates easily and smoothly from the calcareous shell, partly resting on the inner side of the latter. The leucite nucleus is immediately surrounded by a radio-fibrous zone 1—1½ cm. broad, the fibres having a light greenish-grey colour. This fibrous mineral, freed by treatment with acetic acid from intermixed calcium carbonate, gave by analysis 38·6 p.c. SiO_2, 18·4 Al_2O_3, 4·2 FeO, 2·8 CaO, 24·7 MgO, and 11·3 loss (alkalis); showing that it consists of biotite or magnesia mica. This and the garnet and have probably been formed from the leucite and the limestone where they were in contact, under the influence of a very high temperature, the existence of which is shown by the marks of fusion at the boundary between the shell and the nucleus. To account for the occurring of leucite in a shell of limestone is by no means easy, for the latter cannot be regarded as the true matrix of the leucite. The leucitic nuclei of this and the preceding out-cast must rather be regarded as foreign enclosures in the limestone; but it is difficult to see how the limestone can have enclosed the leucites like a plastic mass.

(*c.*) A sanidine stone, containing very numerous crystals of leucite, 5 to 28 mm. in size. The matrix consists of a fine-grained mixture of predominant sanidine, black hornblende, brown garnet, and a small quantity of magnetic iron oxide, also separate tabular crystals of sanidine measuring 20 mm. The leucites are white, with conchoïdal fracture, very fresh, some unusually pure, others showing admixtures of hornblende. They are not sharp-edged, but rather rounded, and are surrounded with a crust 1—1½ mm. thick of small, beautifully formed crystals of sanidine. These appearances might seem to indicate the commencement of a pseudomorphosis of sanidine after leucite, a change which Rammelsberg observed in its completeness in an out-cast very similar to the one under consideration. Closer observation shows, however, that this can hardly be the case. On breaking a leucite nodule from the stone, the sanidine envelope remains behind in the form of a druse lined with the most beautiful crystals of sanidine, firmly attached to the ground-mass, and consisting indeed of purer crystals growing out of it. The separated nodule of leucite is also covered with slender crystals of sanidine firmly implanted on it, and the surface of the leucite itself is developed into innumerable small but well-defined crystals, arranged in parallel rows. Now, when one mineral has been formed from another, or when the process of transformation is in progress, one of the minerals is sure to be found in parts presenting the appearance of the other, and intermediate stages of this transformation are likewise met with. In the present case, however, the closest examination with the microscope shows nothing of the kind. On the contrary, the surface of the leucite nodule is seen to be covered with crystals of leucite and sanidine placed side by side, and both in perfect freshness. Moreover, the stone is perfectly closed, no crack or channel being visible in which alteration of composition might be expected to occur.

For these reasons the author thinks it more probable that when the large rounded crystals began to form, their chemical composition was somewhat different from the typical composition of leucite; perhaps the following:—55·96 p.c. SiO_2, 23·0 Al_2O_3, 21·04 K_2O, which is that of a mixture of $\frac{1}{10}$ sanidine and $\frac{9}{10}$ leucite, and that this mixture after-

wards split up into the two minerals, which indeed occur on the leucite nodules in about this proportion. The leucite, so remarkably distinguished by its shell of sanadine, exhibits nearly the normal composition—

	SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	
Analysis	55·58	23·38	0·26	19·53	1·50	= 100·25
Calculation $K_2O.Al_2O_3.4SiO_2$	55·0	23·5	—	21·5	—	= 100

H. W.

Julianite. By H. Websky (Jahrb. für Mineralogie, 1872, 218).

This mineral occurs in the Frederike Juliane Mine, at Rudelstadt, in Silesia, in small botryoïdal crystalline aggregations, penetrating calcite or covering druses of that mineral. Crystalline characters, indistinct; form, cube in combination with dodecahedron. Hardness very inferior; brittle. Fracture splintery or slightly conchoidal. Specific gravity 5·12. Colour of fresh surface, dark leaden gray, with a slight tinge of red, soon turning black. Composition: copper, 52·298; iron, 0·787; silver, 0·538; sulphur, 26·503; arsenic, 16·782; antimony, 1·421 = 98·329. The deficiency, 1·651 per cent., is believed to be due to loss of arsenic, and calculated as such in the formula—

$$\begin{pmatrix}\frac{9}{10}\mathrm{As}\\ \frac{1}{10}\mathrm{Sb}\end{pmatrix}^2 \begin{pmatrix}\mathrm{Cu}\\ \mathrm{Ag_2}\end{pmatrix}^3 \mathrm{S_6}.$$

Julianite is isomeric and isomorphous with bornite.

W. F.

Lithiophorite. By C. Winckler (Jahrb. für Mineralogie, 1872, 219).

Since Frenzel described this mineral as a manganese ore containing lithia (*Chem Soc. J.*, 1871, 205), Winckler has published two analyses of it—

	K_2O_3.	Na_2O.	BaO.	CaO.	CoO.	NiO.	Bi_2O_3.	CuO.	MnO.	O.	Fe_2O_3.	Al_2O_3.	H_2O.	Sand.	
..	0·73	1·23	2·78	trace	2·42	2·42	trace	1·74	55·12	10·28	1·18	10·54	12·64	—	99·96
..	1·50	1·42	1·26	trace	0·64	0·30	—	0·96	49·87	7·77	2·43	15·53	15·42	3·08	100·18

A list is given of localities of lithiophorite in the district of Schneeberg.

W. F.

Oligoclase, from Wilmington, Delaware. By N. Teclu (Jahrb. für Mineralogie, 1872, 222).

The specimen, which was remarkable for exhibiting cleavage along both faces of the prism, has the following composition:—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	K_2O.
64·75	23·56	2·84	9·04	1·11 = 101·30

W. F.

Manganophyll. By L. J. IGELSTRÖM (Jahrb. für Mineralogie, 1872, 298).

THIS is a new variety of mica from Pajsberg, near Filipstadt in Sweden. It occurs associated with tephroite, hydrotephroite, enematite, magnetite, calcite, garnet, &c.; has a bronze to copper-red colour, forms a pale-red powder, and turns black when heated in the air. Thin plates are transparent, transmitting a rose tint. Crystalline form, hexagonal. It is decomposed by hydrochloric acid, the undissolved silica retaining the form of the original plates. It has the following composition:—

			Oxygen.
Silica	38·50	—	20·53
Alumina	11·00	—	5·15
Manganous oxide	21·40	4·89	15·37
Ferrous oxide	3·78	2·64	
Lime	3·20	0·91	
Magnesia	15·01	6·00	
Potash, with a little soda..	5·51	0·93	
Loss, by ignition	1·60		
	100·00		

This corresponds with the formula $Al_2O_3.\ 3SiO_2 + (3RO.\ SiO_2)$.

The author traces a great resemblance between manganophyll and the alurgite of Breithaupt from St. Marçel, in Piedmont. The latter mineral, which has not yet been quantitatively analysed, has a more decided copper-red colour, and occurs in quartz.

W. F.

Winkworthite. By A. KENNGOTT (Jahrb. für Mineralogie, 1872, 300).

THE author directs attention to the analyses of winkworthite from from Hants Co., Nova Scotia (see *Jour. Chem. Soc.*, 1871, page 320), by Professor How, and maintains that it cannot be regarded as a pure mineral species, but that it is a mixture of about 70 to 80 per cent. of gypsum with 30 to 20 per cent. of silicoborocalcite, the eorolite of Dana.

W. F.

Zennerite. By A. WEISBACH (Jahrbuch fürMineralogie, 1872, 300).

Two new minerals, which have received the names of trögerite and walpurgine, were found last summer in the "Weisser Hirsch" mine, at Neustädt, with a quantity of pitchblende; associated with them was another mineral which, at the time, was believed to be chalcolite,

but is now found to be a new mineral species. Zennerite bears a very great resemblance to chalcolite. Its colour is grass-green, its basal cleavage very complete, the cleavage-planes having a pearly lustre, and it crystallises in the tetragonal system. In hardness it shows no difference from chalcolite, though its specific gravity is somewhat lower, being 3·2. It occurs on ferruginous quartz or ochrey limonite, in crystals partly tabular, partly pyramidal, on which the forms P.oP.∞P are seen. The mean of two analyses is—

Uranium oxide	55·6
Copper oxide	8·7
Arsenic acid	15·1
Water	14·5
Iron oxide	5·2
Lime	1·2
	100·3

which points to the following formula:—

$$3CuO.6UO_3.2As_2O_5.24H_2O,$$

or, the number of molecules of copper oxide, uranium oxide and water being the same, Zennerite contains two molecules of arsenic acid, while chalcolite contains three molecules of phosphoric acid.

W. F.

Eatable Earths of Lapland and Southern Persia. By C. Schmidt (Ann. Chim. Phys. [4], xxvi, 535—9).

The Lapland earth came from the village of Ponoï, 67° 5′ N., 42° 12′ E. It is a light white powder, resembling talc, used in Lapland for mixing with dough for bread. A bed of it 2 or 3 feet thick, exists under the sand and clay of the river Atsche Rjeka. It consists essentially of finely divided potassium silicate, appearing, when magnified 200—300 times, in white non-crystalline scales, but little attacked by hydrochloric or sulphuric acid. It contains in 100 parts, alumina, 40·797; potassium, 45; silica, 9·845·506; water driven off at 100°, 0·260; water removed at a low red heat, 0·835. The author concludes that this so-called edible earth plays only a passive part in alimentation.

The second specimen of earth, from Kirman, in Southern Persia, is known under the name of *G'hel i G'iveh*, and occurs in white and grey lumps, soluble with strong effervescence in dilute nitric and hydrochloric, and in warm acetic acid, leaving a slight residue of silica. It contains in 100 parts, CO_2 45·723, MgO 32·722, CaO 13·235, NaCl 3·542, water at 120°, 1·558, hygroscopic moisture, 1·422. The author considers this earth as a purely mechanical mixture of magnesium and calcium carbonates, with a little magnesium hydrate, acting on the system in the same way as *magnesia alba*. It is in great part soluble in carbonic acid water.

C. G. S.

The Earth-Salts of Bellary (India). By E. Nicholson (Chemical News, xxvi, 221).

Organic Chemistry.

Changes in the Position of Hydrogen-Atoms on the Carbon-Skeleton of Organic Bodies. By W. Heintz (Ann. Chem. Pharm., clxv, 33—38).

In the author's opinion the supposition that an atom of hydrogen can become detached from a carbon-atom and attach itself to another carbon-atom in the same molecule, is not supported by the facts at present known.

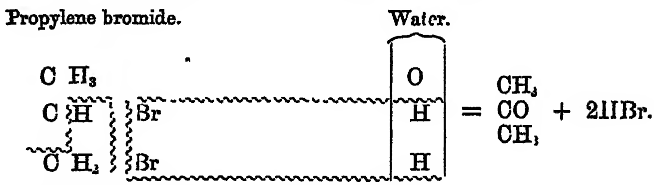
The first case considered is the formation of isopropyl alcohol by the decomposition of propylamine nitrite. This reaction is represented by Linnemann in the following manner:—

$$\mathrm{CH_3{-}CHH{-}CH_2}\overset{\mathrm{H}}{>}\underset{\underset{\mathrm{O{=}N{=}O}}{|}}{\mathrm{N}}\!<\!\begin{matrix}\mathrm{H}\\\mathrm{H}\end{matrix} = \mathrm{CH_3{-}CH\,\underset{O}{H}\,{-}CH_3} + \begin{matrix}\mathrm{N}\\\mathrm{N}\end{matrix} + \begin{matrix}\mathrm{H}\\\mathrm{H}\\\mathrm{O}\end{matrix}$$

Linneman considers that in this case two hydrogen-atoms belonging to the ammonium unite with one of the oxygen-atoms of the nitryl, forming water, while the two nitrogen-atoms unite, forming a molecule of that substance, and the remaining oxygen-atom of the nitryl moves towards the middle carbon-atom, and unites with one of its hydrogen-atoms.

The author points out that in this case no hydrogen travels from one carbon-atom to another, as the atom of oxygen merely takes a place between the middle carbon-atom and one of its hydrogen-atoms.

The next case considered is the formation of hydriodic acid and acetone by the action of water on propylene bromide. This reaction is represented by Linnemann in the following manner:—



Linnemann considers that in this case the two hydrogen-atoms of the water unite with the two bromine-atoms, forming hydrobromic acid, and that the oxygen of the water unites with the middle carbon-atom of the propylene, at the same time driving its hydrogen-atom to the unsaturated carbon-atom standing next. The author considers that this reaction may be satisfactorily explained by assuming that the hydrogen and bromine combined with the middle carbon-atom unite, forming one molecule of hydrobromic acid, while one hydrogen-atom of the water unites with the remaining atom of bromine, and the second hydrogen-atom of the water unites with the exterior carbon-atom, which has just lost an atom of bromine, the oxygen, as before, uniting

with the middle carbon-atom. This view is illustrated by the following formula:—

$$\begin{array}{lcl} \text{Propylene bromide.} & & \text{Water.} \\ C\ H_3 & & O \\ C\ \{H\ \ Br\} & & \\ C\ H_2\ \{Br & & H\}\ H \end{array}$$

The author's view is confirmed by the fact that monobromopropylene, when heated with water, yields acetone and hydrobromic acid.

$$\begin{array}{lll} \text{Monobromopropylene.} & \text{Water.} & \\ C\ H_3 & & \\ C\ \{Br\ \ + & H\}\quad O & = \begin{array}{c} CH_3 \\ CO \\ CH_3 \end{array} + HBr. \\ C\ \ H_2 & H & \end{array}$$

In this case the middle carbon-atom not being united with any hydrogen, it is clear that the exterior unsaturated carbon-atom must receive its third hydrogen-atom from the water.

Recently Linnemann has called attention to a case of the change in question, which appears incontrovertible (*Ann. Chem. Pharm.*, clxii, 19). When iodine monochloride acts on isobutyl iodide, iodine is liberated, together with the chloride of tertiary butyl.

$$\begin{array}{llll} \text{Isobutyl iodide.} & & \text{Iodine monochloride.} & \\ C\ H_3 & & & \\ C\ H_3 & + & Cl & = I_2 + \begin{array}{c} CH_3 \\ CH_3 \\ CCl \\ CH_3. \end{array} \\ C\ \{H\} & & & \\ C\ H_2\ \{I & & I\} & \end{array}$$

The author admits that in this case an atom of hydrogen passes from one carbon-atom to another, but he maintains that the reaction takes place by two stages: the first consisting of the formation of hydrochloric acid, a molecule of iodine, and free butylene; and the second consisting of a union of the hydrochloric acid and the butylene.

$$\text{1st stage}\quad \begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ CH \\ | \\ CH_2I \end{array} + \begin{array}{c} Cl \\ I \end{array} = I_2 + HCl + \begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ C \\ \| \\ CH_2. \end{array}$$

$$\text{2nd stage}\quad \begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ C \\ \| \\ CH_2 \end{array} + \begin{array}{c} Cl \\ H \end{array} = \begin{array}{c} CH_3\ \ CH_3 \\ \diagdown\ \diagup \\ CCl \\ | \\ CH_3. \end{array}$$

T. B.

On Dichlorethyl Oxide. By Haruthiun Abeljanz (Ann. Chem. Pharm., clxiv, 197—228).

The action of chlorine upon ethylic ether furnishes a body which is isomeric with ethylidene oxychloride. This substance, according to Lieben, splits, under the influence of alkalis, into alcohol and acetic acid. In studying this body, Lieben also came to the conclusion that the chlorine is divided unsymmetrically, and that the formula, $\left.\begin{matrix}C_2H_3Cl_2\\C_2H_5\end{matrix}\right\}O$ must be adopted.

By treating dichlor-ethyl oxide with phosphorus tribromide, he always obtained ethyl bromide, thus showing that in this substance, and hence also in its derivatives, in which the chlorine is wholly or partly replaced by other groups, ethyl as such must exist unaltered, the chlorine-atoms belonging to one only of the two ethyl groups.

Conclusive evidence of the same fact may also be found in the formation of ethyl alcohol by decomposition of dichlorethyl oxide by water, and no less in the production of a true hexyl iodide, together with ethyl iodide, by the action of hydriodic acid on diethylated ethyl oxide—

$$\left\{\begin{matrix}C_2H_3(C_2H_5)_2\\OC_2H_5\end{matrix}\right. + 2HI = C_2H_3(C_2H_5)_2I + C_2H_5I + H_2O.$$

The formula, $\left\{\begin{matrix}C_2H_3Cl_2\\OC_2H_5\end{matrix}\right.$ for dichlor-ethyl oxide, may therefore be considered established. It now remains to be determined in what order the chlorine is attached to the carbon-atoms of the ethyl group, and, in fact, which of the three possible formulæ—

$$\begin{matrix}\text{I.} & & \text{II.} & & \text{III.}\\ \left\{\begin{matrix}CHCl_2\\CH_2\\OC_2H_5\end{matrix}\right. & & \left\{\begin{matrix}CH_3\\CCl_2\\OC_2H_5\end{matrix}\right. & \text{or} & \left\{\begin{matrix}CH_2Cl\\CHCl\\OC_2H_5\end{matrix}\right.\end{matrix}$$

should be adopted.

The experiments of Lieben leave this to a certain extent undecided, one observation, however, the supposed production of acetic acid by the action of potassium hydrate, pointing to formula II, by which alone the reaction can be explained:

$$\left\{\begin{matrix}CH_3\\CCl_2\\OC_2H_5\end{matrix}\right. + 3KOH = 2KCl + \left\{\begin{matrix}CH_3\\CO.OK\end{matrix}\right. + HOC_2H_5 + H_2O.$$

The author undertook his experiments upon dichlorethyl oxide in the first place with the hope of producing by the action of phosphorus pentachloride, the trichlorethane $CH_3.CCl_3$, intending to make that body the starting point of a series of researches. In this hope, however, he was disappointed, but he obtained instead some important information as to the constitution of dichlorethyl oxide.

The dichlorethyl oxide employed was prepared according to Lieben's directions, and purified with great care by repeated distillation.

Action of Phosphorus Pentachloride on Dichlorethyl Oxide.—The assertion of Lieben that dichlorethyl oxide is not acted upon by phosphorus pentachloride in the cold, or at a gentle heat, is contradicted by the author.

The two substances, brought together in the proportion of a molecule of each, react pretty briskly, the temperature rising to 65° or 70°. The experiment was performed in a retort, connected with an upright condenser, and this again with a series of Woulff's bottles, leading finally to a well cooled Liebig's condenser, terminating in a U-tube surrounded by ice and salt. A small quantity of hydrochloric acid was collected in the Woulff's bottles, and in the U-tube a considerable amount of pure ethyl chloride. The residue contained phosphorus trichloride and oxychloride, and when submitted to distillation, gave below 130° a liquid, which, when treated with water, furnished a large quantity of hydrochloric acid, and a solution possessing a peculiar aldehydic smell. With the view of isolating this aldehydic body, the solution was neutralised by boiling with lead oxide and distilled. A colourless oil was deposited from the distillate, but as it was decomposed by redistillation, the whole was oxidised by heating it with excess of silver oxide. After removal of the reduced silver and the silver chloride, which had been simultaneously produced, the acid was converted into zinc salt and analysed. The physical properties and composition of this compound showed that it was zinc glycollate.

The products of the action of phosphorus pentachloride boiling above 130°, consisted chiefly of unchanged dichlorethyl oxide.

This formation of glycollic acid from an aldehydic body is distinctly in opposition to Lieben's formula for dichlorethyl oxide, according to which acetic acid only could have been obtained by the action of metallic oxides. An aldehyde, to yield glycollic acid, must contain 3 atoms of hydrogen, which must be divided between two carbon-atoms, $\left\{\begin{matrix} CH_2 \\ CH \cdot \end{matrix}\right.$

Dichlorethyl oxide must therefore consist at least partly of the compound, $\left\{\begin{matrix} CH_2Cl \\ CHCl \, . \\ OC_2H_5 \end{matrix}\right.$

It might possibly contain also the isomeric body, $\left\{\begin{matrix} CH_3 \\ CCl_2 \\ OC_2H_5 \end{matrix}\right.$, but in that case acetic acid would have been formed by boiling with lead oxide. Acetic acid, however, could not be detected in any portion of the lead salts.

The principal reaction between phosphorus pentachloride and dichlorethyl oxide is, therefore, represented according to the following equation:—

$$\left\{\begin{matrix} CH_2Cl \\ CHCl \\ OC_2H_5 \end{matrix}\right. + PCl_5 = POCl_3 + C_2H_5Cl + \left\{\begin{matrix} CH_2Cl \\ CHCl_2. \end{matrix}\right.$$

The last body by boiling with lead oxide yields monochloraldehyde—

$$\left\{\begin{array}{l}CH_2Cl\\CHCl_2\end{array}\right. + PbO = \left\{\begin{array}{l}CH_2Cl\\CHO\end{array}\right. + PbCl_2,$$

And this afterwards gives glycollic acid, silver, and silver chloride—

$$\left\{\begin{array}{l}CH_2Cl\\COH\end{array}\right. + 4AgOH = AgCl + Ag_2 + 2H_2O + \left\{\begin{array}{l}CH_2OH\\COOAg.\end{array}\right.$$

In order to exclude the complication introduced by the chlorine-substituting action of phosphorus pentachloride, the author has studied *the decomposition of dichlorethyl oxide by water.*

Dichlorethyl oxide heated in sealed tubes with seven or eight times its volume of water to 115°—120°, but not higher, gave a colourless homogeneous solution. The liquid contained hydrochloric acid, ethyl alcohol, and a mixture of aldehydes, among which chloraldehyde was identified by treating with silver oxide and analysing the zinc salt of the resulting glycollic acid. Another portion of the watery solution of the aldehyde was exposed for a week to the air and then evaporated. A mixture of two kinds of crystals was thus obtained, which when separated and recrystallised, turned out to be monochloracetic acid (from the chloraldehyde) and glycollic acid. The latter could only have resulted from the oxidation of the hitherto unknown oxaldehyde, $\left\{\begin{array}{l}CH_2.OH\\CHO\end{array}\right.$, which may be regarded as the aldehyde of glycollic acid.

The oily body which was produced in small quantity by distillation of the original acid solution, is probably a hydroxyl-chlor-ethyl oxide, $\left\{\begin{array}{l}C_2H_3Cl(OH)\\O.C_2H_5\end{array}\right.$.

From these results the principal reaction between water and dichlorethyl oxide, may be represented as follows:—

$$\underset{\text{Dichlorethyl oxide.}}{\left\{\begin{array}{l}CH_2Cl\\CHCl\\OC_2H_5\end{array}\right.} + H_2O = \underset{\text{Chloraldehyde.}}{\left\{\begin{array}{l}CH_2Cl\\COH\end{array}\right.} + \underset{\text{Alcohol.}}{HOC_2H_5} + HCl.$$

The oxaldehyde results from the subsequent decomposition of the chloraldehyde by water—

$$\left\{\begin{array}{l}CH_2Cl\\COH\end{array}\right. + H_2O = \underset{\text{Oxaldehyde.}}{\left\{\begin{array}{l}CH_2HO\\COH\end{array}\right.} + HCl.$$

Decomposition of Dichlorethyl oxide by Alkalis.—The results were similar to those obtained in the decomposition by water. Alcohol, chloraldehyde, and two other chlorinated bodies are formed. The former of these possesses the composition of a hydroxyl-chlorethyl oxide $\left\{\begin{array}{l}CH_2Cl\\CH(OH)(OC_2H_5)\end{array}\right.$, and boils at about 153°: the latter is a condensation-product $\left\{\begin{array}{l}C_2H_3Cl.OC_2H_5\\O\\C_2H_3Cl.OC_2H_5\end{array}\right.$, boiling at 163°—165°, and is iden-

tical with the body observed by Jacobsen as a product of the decomposition of dichlorethyl oxide with water.

The question still remained whether, under certain circumstances, dichlorethyl oxide may not be converted into acetic acid as stated by Lieben.

The author therefore examined very carefully the saline residue of the reaction with potash, but could find only a small quantity of formic but no acetic acid.

Besides the reaction in which the hydroxyl-chlorethyl oxide, already described, is the principal product, another which furnishes an isomeride of that body occurs at the same time:—

$$\left\{\begin{array}{l} CH_2Cl \\ CHCl \\ OC_2H_5 \end{array}\right. + KOH = KCl + \left\{\begin{array}{l} CH_2(OH) \\ CHCl \\ OC_2H_5. \end{array}\right.$$

This substance is not susceptible of condensation, but when treated with concentrated sulphuric acid furnishes hydrochloric acid, sulphethylic acid, and oxaldehyde:—

$$\left\{\begin{array}{l} CH_2OH \\ CHCl \\ OC_2H_5 \end{array}\right. + H_2SO_4 = HC_2H_5SO_4 + HCl + \left\{\begin{array}{l} CH_2OH \\ CHO, \end{array}\right.$$

together with a small quantity of a body which is the analogue of ethylidene oxychloride, and results from a secondary reaction between the hydrochloric acid and the oxaldehyde:—

$$2\left\{\begin{array}{l} CH_2OH \\ CHO \end{array}\right. + 2HCl = \left\{\begin{array}{l} CH_2OH \\ CHCl \\ O \\ CHCl \\ CH_2OH \end{array}\right. + H_2O.$$

The condensation-product, $C_8H_{16}Cl_2O_3$, which had been obtained from dichlorethyl oxide by the action of potash gives scarcely any hydrochloric acid when treated with sulphuric acid, but forms chloraldehyde, water, and ethylsulphuric acid.

The chloraldehyde could not be purified by fractional distillation, but when oxidised by silver oxide it gives glycollic acid; on exposure to the air it leaves crystals of monochloracetic acid. It unites with bisulphite of soda, and ammonia passed into its ethereal solution produces a crystalline compound in large pearly tables, melting at about 130°.

As the main result of the foregoing experiments the author considers that the formula $\left\{\begin{array}{l} CH_2Cl \\ CHCl, \\ OC_2H_5 \end{array}\right.$ must be taken to represent the constitution of dichlorinated ethyl oxide. A corresponding modification must therefore be adopted in the formulæ of all its derivatives.

W. A. T.

On Trichloracetal and Tetrachlorethyl Oxide. By E. PATERNÒ and G. PISATI (Gazzetta Chimica Italiana, ii, 333—338).

WURTZ and Vogt have lately shown (*Compt. rend.*, lxxiv, 777; *Chem. Soc. J.*, 1872, 610) that when tetrachlorethyl oxide (prepared, according to Henry's method, by the action of phosphorus pentachloride on chloral alcoholate) is heated with alcohol in a sealed tube, a liquid is obtained which boils between 199° and 201°, and has the composition of trichloracetal. On the other hand, Paternò having many years ago obtained a substance which appeared to have the composition of trichloracetal, but differed essentially in its physical properties from the compound described by Wurtz and Vogt, it was considered important to resume the examination of these bodies.

1. *Tetrachlorethyl oxide*, $(C_2HCl_4)_2O$, was prepared by Henry's process, and exhibited for the most part the properties described by that chemist; it boiled at 189·7° under a reduced pressure of 857 5 mm., and had a density of 1·4370 at 0°, 1·4182 at 15·2°, 1·3055 at 99·9°. Heated with alcohol in sealed tubes for several hours in a bath of salt-water, it yielded the *trichloracetal* of Wurtz and Vogt, which is a transparent, very mobile liquid, having a pleasant odour, much like that of dichloracetal, boiling at 204·8° (corr.) under the pressure of 758·9 mm., and having a density of 1·2813 at 0°, 1·2655 at 22·2°, 1·1617 at 99·96°. Its analysis gave numbers agreeing with the formula $C_2Cl_3H(C_2H_5O)_2$.

2. Paternò's *trichloracetal* was obtained in small quantity as a secondary product in the preparation of dichloracetal by the action of chlorine on common alcohol (*Compt. rend.*, lxvii, 765). The authors in repeating the experiment were likewise unable to obtain more than a small quantity of the product. It is solid at ordinary temperatures, melts at 72°—74°, but apparently begins to decompose at the same time, so that the melting point cannot be determined with accuracy.

The mean results of the analysis of the liquid and solid compounds show that they are isomeric:—

	Calculated.		*Liquid.* Wurtz & Vogt.	*Solid.* Paternò & Pisati.
C_6	72·0	32·52	32·50	32·13
H_{11} ..	11·0	4·96	4·93	4·97
Cl_3 ..	106·5	48·05	48·33	48·18
O_2	32·0	14·47		
	221·5	100·00		

The mode of formation of the liquid trichloracetal shows that it has the constitution $CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.$:—

$$CCl_3.CH\left\{\begin{matrix}OC_2H_5\\Cl\end{matrix}\right. + HOC_2H_5 = HCl + CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right.,$$

which is confirmed by its mode of decomposition when heated with water or with sulphuric acid, the products of which, according to Wurtz and Vogt are alcohol and chloral:—

$$CCl_3.CH\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right. + H_2O = 2HOC_2H_5 + CCl_3.CHO.$$

The solid trichloracetal appears also to yield chloral when heated with sulphuric acid; at all events, the distillate when heated with potash and a small quantity of aniline, gives off the characteristic odour of the carbamines (isocyanides), a result which indicates the formation of chloroform, and thereby tends to show that the product of the action of sulphuric acid on trichloracetal is really chloral. Nevertheless the authors do not regard their experiments (which were made on a small quantity of substance) as quite conclusive on this point, but think it possible that the product of this reaction may be dichloraldehyde, $C_2Cl_2H.CHO$. In this case, the constitution of solid trichloracetal might be represented by the formula,

$$CCl_2H.CH\left\{\begin{matrix}OC_2H_4Cl\\OC\,H_5\end{matrix}\right., \text{ or by } CCl_2H.CCl\left\{\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix}\right..$$

3. Tetrachlorethyl oxide is transformed into trichloracetal, not only by alcohol, but likewise, though much less sharply, by sodium ethylate, or a very strong alcoholic solution of potash. If, however, the same compound be treated with a 10 p. c. solution of potassium hydrate in absolute alcohol, a totally different reaction takes place, a molecule of hydrochloric acid being eliminated, and a compound being formed which appears to have the constitution $CCl_2{=}CCl{-}OC_2H_5$. The reaction takes place at ordinary temperatures, with abundant deposition of potassium chloride. On dissolving out this salt by water, an oily liquid separates, which, when dried and purified by fractional distillation, boils at 154·8° (corr.) under the pressure of 755 mm., has a density of 1·5725 at 0° and 1·2354 at 99 9°, and gives by analysis 26·45 to 27·53 p. c. carbon, 2·93 to 2·98 hydrogen, and 59·55 to 60·59 chlorine, the formula $C_4H_5Cl_3O$ requiring 27·37 p. c. C., 2·85 H., and 60·65 Cl.

This compound unites directly with bromine, the combination being attended with rise of temperature, and forms a liquid which, after washing with water and sodium carbonate, is perfectly colourless; it is much heavier than water, is decomposed by distillation under ordinary pressure, but distils without alteration under a pressure of 4 centimeters, and boils at about 135°; in a mixture of snow and salt it solidifies to a crystalline mass which melts at the temperature of the air.

This chlorobrominated compound probably has the constitution represented by the formula $CCl_2Br{-}CClBr.O.C_2H_5$. It is violently attacked by concentrated alcoholic potash, yielding a heavy oil which may be separated by distillation with aqueous vapour into the original chlorinated compound and a substance which is solid at the ordinary temperature (24°), and well crystallised. The authors are engaged with the further examination of these products.

H. W.

Chloro-derivatives of Acetone. By C. Bischoff (Deut. Chem. Ges. Ber., v, 863—867).

Riche obtained, by the action of the galvanic current on a mixture of acetone and hydrochloric acid, *monochloracetone* boiling at 117°; but

Borsche and Fittig doubt the existence of this compound, because by acting on well cooled acetone they always obtained a dichloracetone boiling at 120°; whilst Kriwaksin, on repeating the experiments of these chemists, could only obtain monochloracetone boiling at 120°—125°, together with products of condensation. The author's experiments are in accordance with the latter investigation.

Monochloracetone boils at 118°—121°. By gently heating a mixture of this compound with strong hydrocyanic acid and alcohol for 24 hours, and evaporating the liquid, the compound, $C\left\{\begin{array}{l}CH_2Cl\\CN\\OH\\CH_3\end{array}\right.$, is left behind as a thin oily liquid, which when heated with hydrochloric acid, yields ammonium chloride and *monochloracetonic acid*, $C\left\{\begin{array}{l}CH_2Cl\\CO.OH\\OH\\CH_3\end{array}\right.$, crystallising in prisms which have a pure sour taste. The sodium salt is a deliquescent, crystalline mass; the ammonium salt crystallises in prisms, and the lead salt is obtained by evaporating an aqueous solution as an amorphous transparent mass. The ethylic ether is an oily liquid having a faint but agreeable odour, which cannot be distilled.

The chlorine in monochloracetonic acid can be replaced by cyanogen, and thus the nitrile of an acid is produced which is probably an isomeride of oxypyrotartaric acid. C. S.

Researches on Dulcite and on Sugars in General.

By G. Bouchardat (Ann. Chim. Phys. [4], xlvii, 68—109).

This paper is divided into the following sections:—

1. Artificial formation of dulcite by the hydrogenation of galactose and milk-sugar.
2. Presence of milk-sugar in plants.
3. Formation of isopropylic, ethylic, and hexylic alcohols by hydrogenation of the glucoses.
4. Transformation of acetone into a hydrocarbon isomeric with hexylene hydride.

The results have been already given in preliminary notices in the *Comptes rendus de l'Académie*, abstracts of which will be found in the last two volumes of this *Journal*, 1871, pp. 810, 915; 1872, pp. 399, 400, 409, 691, 1093. H. W.

Neutral Compounds derived from Mannite. By G. Bouchardat

(Compt. rend., lxxv, 1187—1190).

Dichloromannite, $C_6H_2(H_2O)_4(HCl)_2$ $\left(\text{or, } C_6H_8\left\{\begin{array}{l}(OH)_4\\Cl_2\end{array}\right.\right)$ is prepared by heating together 15 parts of hydrochloric acid solution saturated at 0° C., and one part of mannite in a sealed tube at 100°, for six hours only, since a longer exposure appears to produce dichloromannitan (*Ann. Chim. Phys.* [3], xlvii, 334). After drying over quicklime and

oil of vitriol for about a month, long scales of a light yellow colour are separated, which are dissolved in cold water and recrystallised. The aqueous solution is neutral and tasteless, and is not precipitated by silver nitrate. Dichloromannite is insoluble in absolute alcohol and in ether. It melts at 174°, being at the same time decomposed; at a higher temperature it volatilises completely. Its vapour burns with a green-edged flame. Boiling water or concentrated solution of alkali rapidly decomposes it into *monochloromannitan*, thus :—$C_6H_8\begin{cases}(OH)_4\\Cl_2\end{cases} - HCl = C_6H_8\begin{cases}(OH)_3\\O\\Cl\end{cases}$. This reaction appears to be general with the polyatomic haloïd ethers; *e.g.*, dichlorhydrin is converted by the same means into epichlorhydrin.

Monochloromannitan thus formed is a neutral, slightly bitter substance, very soluble in water, alcohol, and ether. By prolonged agitation with water it is converted into mannitan.

Nitrosulphuric acid converts dichloromannite into dichloro-tetranitromannite, $C_6H_2(NHO_3)_4(HCl)_2$ $\left(\text{or, } C_6H_8\begin{cases}(NO_3)_4\\Cl_2\end{cases}\right)$, which is insoluble in water, but soluble in boiling alcohol, separating from that solution, on cooling, in fine needles. This substance is not easily explosive, notwithstanding its composition; it is, in fact, more stable than dichloromannite.

Dibromomannite, $C_6H_2(H_2O)_4(HBr)_2$ $\left(\text{or } C_6H_8\begin{cases}(OH)_4\\Br_2\end{cases}\right)$ is prepared in a similar way to the analogous chlorine-compound, the mannite and hydrobromic acid, being heated together for two hours only. Crystals appear after a considerable length of time, and are purified by rapid solution in hot water and cooling. Dibromomannite is tasteless, scentless, insoluble in cold water, alcohol, or ether, but soluble in warm water, and in concentrated hydrobromic acid solution. It crystallises in small colourless plates, melting, with decomposition, at 178°.

Boiling water transforms dibromomannite into *monobromomannitan*, $C_6H_2(H_2O)_4(HBr)$ $\left(\text{or } C_6H_8\begin{cases}(OH)_3\\O\\Br\end{cases}\right)$, which is a neutral, slightly bitter substance, very soluble in alcohol or ether, and melting at 100°. Its solution is not precipitated by silver nitrate. Long-continued boiling with water converts it into mannite.

Nitrosulphuric acid converts dibromomannite into dibromo-tetranitromannite, $C_6H_2(NHO_3)_4(HBr)_2$ $\left(\text{or } C_6H_8\begin{cases}(NO_3)_4\\Br_2\end{cases}\right)$, which crystallises in long needles, insoluble in water and in cold alcohol, but soluble in the latter when it is heated.

The above compounds are isomeric with the dulcite-ethers already described by the author; they give similar reactions, with one exception, by which the two series may be distinguished, viz., when treated with alkaline hydrates, the ethers above described furnish mannitan, whereas those of the dulcite series yield dulcitan, which may be recognised by converting it into mucic acid. B. J. G.

Researches on Santonin. By L. DE ST. MARTIN (Compt. rend., lxxv, 1190—1192).

DESIRING to ascertain whether santonin, the active principle of *Semen contra*, be really a phenol, as Berthelot (*Traité élémentaire de Chimie Organique*) considered it, the author began by attempting its gradual deoxidation. If the formula of santonin be $C_{15}H_{18}O_3$, there should be obtained by this means—(1.) A diatomic phenol, $C_{15}H_{18}O_2$; (2.) a monatomic phenol, $C_{15}H_{18}O$; (3.) a hydrocarbon, $C_{15}H_{18} = C_{10}(H_7.C_5H_{11})$, or amyl-naphthalene. The second of these is the only one yet obtained, and is formed when one part of santonin and four parts of zinc are heated in a current of hydrogen. A brownish-yellow liquid is obtained, in which, after some days, needle-shaped crystals begin to form. These are purified by distillation at 350°, when two isomeric bodies neutral to litmus are obtained, the one crystalline and the other liquid, for both of which the name of *santonol* is proposed. *Crystalline santonol* is similar in appearance to stearin, and melts at 135°. It is insoluble in water, and very soluble in alcohol or ether. Sulphuric acid forms with it a sulpho-conjugated acid, the barium salt of which is soluble. Santonol dissolves when it is mixed with a moderate quantity of potash solution, but a large excess of potash gives rise to *potassium santonolate*, which is an oil yielding santonol on treatment with an acid. These and other properties not mentioned prove santonol to be a phenol. (It will, however, be noticed that its formula is not like the general formula of phenols.)

Liquid santonol is very changeable on exposure to air. It is, like the solid with which it is saturated, insoluble in water, but soluble in alcohol or ether.

B. J. G.

Production of Furfurol by the Action of Superheated Water upon Wood. By C. GREVILLE WILLIAMS (Chemical News, xxvi, 231, 247 and 293).

WHEN fir-wood is heated with water in a closed vessel, and a pressure of 100 lbs. to the inch maintained for a considerable time, an acid liquor is obtained, from which, by repeated rectification, two principal products may be separated. These are methylic alcohol and an oil, the yield of the latter from 100 lbs. of wood being 10 ounces.

The oil was not uniform in composition, and had not a constant boiling-point. On immersion in a freezing mixture it separated into two layers. The lower layer had a sp. gr. of 1·0784 at 11°, and was suspected to consist mainly of furfurol; it was therefore rectified, and the fraction boiling between 163° and 171° oxidised by treatment with caustic potash.

The crystals so obtained were analysed, and found to consist of potassium pyromucate, $KC_5H_3O_3$.

To confirm this result, a portion of the crude oil was converted into the corresponding amide, and the crystalline mass purified and analysed. Results were obtained which proved that the crystals consisted of pure furfuramide, $C_{15}H_{12}N_2O_3$.

A mean of four experiments showed that 100 parts of crude oil gave 39·3 of furfuramide, corresponding to 42·3 per cent. of furfurol. Hugo Müller corroborates the foregoing results. Having operated in a similar series of experiments with bamboo-wood, he obtained an appreciable quantity of a heavy oily liquid, which exhibited all the properties of furfurol, and produced, on the addition of ammonia, the well-characterised furfuramide. Müller does not think that the production of furfurol is due to the action of the organic acids which are simultaneously or previously formed; at the same time he mentions that when the wood is treated with caustic soda-lye instead of water, the formation of furfurol does not appear to take place.

Furfurol may also be obtained by the action of high-pressure steam upon wood. The apparatus used (a figure of which is given) consists of an autoclave capable of withstanding a pressure of 500 lbs. to the square inch, within which is placed a cylinder of perforated metal filled with sawdust and standing on a perforated shelf; the bottom of the autoclave is covered with a layer of water not reaching to the shelf. The vessel having been tightly closed, is heated in an oil-bath to 198° C. for three or four hours, after which it is left to cool till the pressure has completely gone down. The autoclave is then opened and connected with a condenser, and heated till about three-fourths of the water present has distilled over. The watery distillate thus obtained smells strongly of furfurol, and when mixed with ammonia yields crystals of furfuramide.

It appears then that furfurol may be produced from wood by the action either of water or of steam at high temperatures and pressures. The author finds, however, that it is not produced by distilling sawdust with water under the ordinary pressure.

J. W.

On some Derivatives of Mucic Acid. By MAX KÖTTNITZ (J. pr. Chem. [2], vi, 136—156).

THE author begins this memoir with a historical account of pyrrol (C_4H_5N), a derivative of mucic acid hitherto little studied.

Schwanert (*Ann. Chem. Pharm.*, cxvi, 271), found that pyrrol is one of the products of the dry distillation of ammonium mucate. Lubavin (*Deut. Chem. Ges. Ber.*, ii, 99) succeeded in replacing one atom of hydrogen in pyrrol by ethyl, but left it doubtful whether this substituted atom is in direct combination with carbon or with nitrogen. With the view of settling this question, the author has endeavoured to obtain a substituted pyrrol by the dry distillation of a substituted ammonium salt of mucic acid. For this purpose he prepared—

Phenylamine Mucate, $C_6H_{10}O_8(C_6H_5H_2N)_2$. This body is best obtained as follows:—A mixture of mucic acid with a relatively large quantity of water is heated to boiling in a capacious flask, and aniline is added in small portions, with frequent shaking, till the liquid is nearly clear. The solution is filtered hot and left to crystallise. After thorough washing with water and recrystallisation from boiling water, the product is pure neutral phenylamine mucate.

The same salt is formed, together with phenylmucamide, by heating mucic acid for a sufficient time with excess of aniline—

$$2C_6H_{10}O_8 + 4C_6H_7N = C_6H_{10}O_8(C_6H_7N)_2 + C_6H_8O_6(C_6H_5HN)_2 + 2H_2O.$$

Phenylamine mucate forms feebly yellow crystals, which dissolve in water and lose phenylamine on prolonged heating therewith, apparently without forming an acid salt. It is insoluble in boiling alcohol, but gives off the whole of its phenylamine on prolonged treatment with the boiling liquid. When heated with alkalis it yields alkaline mucates, phenylamine being set free. Heated in an air-bath it loses water, and is converted into phenylmucamide—

$$C_6H_{10}O_8(C_6H_5H_2N)_2 - 2H_2O = C_6H_8O_6(C_6H_5HN)_2.$$

By dry distillation it is resolved into phenylamine, water, carbon dioxide, and phenylpyrrol.

Phenylmucamide, $\left.\begin{matrix} C_6H_5H \\ C_6H_8O_6 \\ C_6H_5H \end{matrix}\right\} N_2$. The formation of this body in two ways has already been mentioned. It is best prepared, however, by the action of phenylamine on an ether of mucic acid. The author employs ethyl mucate, prepared thus:—1 part of mucic acid is heated with 4 parts of sulphuric acid till the mixture begins to blacken. On cooling, 4 parts of absolute alcohol are added, and after 24 hours the whole is diluted with spirit, filtered, washed thoroughly with spirit, and afterwards exhausted with boiling water to remove undecomposed mucic acid.

Phenylmucamide forms small, very thin, white laminæ, which are quite insoluble in water, alcohol, ether, benzene, carbon disulphide, glycerin, and dilute mineral acids. It is decomposed by boiling with strong potash, phenylamine being separated. Concentrated sulphuric acid converts it into a black mass. Fuming nitric acid dissolves it, forming a yellow solution, from which water throws down a yellow body, probably a nitro-substitution product.

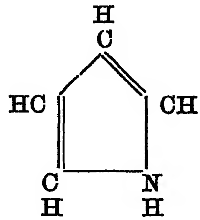
The author endeavoured in vain to prepare the imide corresponding to the foregoing body, namely, *phenylmucimide*, $C_6H_8O_6 \cdot C_6H_5N$.

Phenylpyrrol, $\left.\begin{matrix} C_4H_4 \\ C_6H_5 \end{matrix}\right\} N$. This body is obtained pure by treating the mass formed by the dry distillation of phenylamine mucate with very weak hydrochloric acid to remove phenylamine, washing with water till the mass is free from acid, crystallising repeatedly, and drying over sulphuric acid.

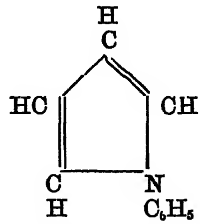
Phenylpyrrol forms fine, white, nacreous, thin scales, which acquire a reddish colour on prolonged contact with air. It has an aromatic camphor-like odour; melts at 62°; is soluble in alcohol, ether, benzene, and chloroform, and crystallises from the solutions; insoluble in cold water, and melts to a colourless transparent oil on warming therewith. It is not acted upon by mineral acids or alkalis

The formation of phenylpyrrol from phenylamine mucate may be regarded as a proof of the correctness of the constitutional formula proposed for pyrrol by Baeyer and Emmerling (*Chem. Centr.*, 1870,

437), according to which, one atom of hydrogen is in direct combination with nitrogen. It is evident that the phenylamine residue, C_6H_5N, unites with the group C_4H_4 of the mucic acid to form phenylpyrrol—



Pyrrol.



Phenylpyrrol.

Phenylpyrrol-mercuric Chloride, $2\left(\left.\begin{matrix}C_4H_4\\C_6H_5\end{matrix}\right\}N\right).HgCl_2$. Formed by adding mercuric chloride dissolved in alcohol to an alcoholic solution of phenylpyrrol. It is white, and less soluble in boiling alcohol than phenylpyrrol. It is soluble also in chloroform and carbon disulphide, slightly soluble in boiling water, but insoluble in benzene, in which phenylpyrrol dissolves very easily. When boiled with potash it does not melt, as does phenylpyrrol, but turns yellow, without dissolving. It dissolves in hydrochloric acid, with yellow colour.

Toluidine Mucate, $C_6H_{10}O_8(C_7H_9N)_2$. This body is prepared by the author in the same way as phenylamine mucate. It forms yellowish crystals soluble in boiling water, though less freely so than the phenyl compound. The aqueous solution loses toluidine when long boiled. It is insoluble in alcohol and ether, but gives off toluidine when boiled therewith. It is converted by prolonged heating in an air bath into tolylmucamide.

It is remarkable that toluidine mucate when submitted to dry distillation does not yield a substituted pyrrol, as does phenylamine mucate. The chief product is a body having the empirical formula $C_{18}H_{18}N_2$, but owing to its indifference towards reagents the author has not been able to arrive at any definite notion of its constitution. It forms very fine, white, nacreous scales, which are easily soluble in alcohol, benzene, and carbon disulphide. It possesses a strong aromatic odour, and is highly electric, so that when rubbed in an agate mortar the powder flies off in all directions.

Tolylmucamide, $\left.\begin{matrix}C_7H_7H\\C_6H_8O_6\\C_7H_7H\end{matrix}\right\}N_2$. This body is best obtained by the action of toluidine on an ether of mucic acid, as in the case of the corresponding phenyl-compound. It forms white thin laminæ, resembling the phenyl-compound in their insolubility. It is decomposed by strong potash, toluidine being set free. J. R.

Supersaturated Solutions of Lactates. By L. C. de Coppet (Ann. Chim. Phys. [4], xxvi, 539—544).

A hot saturated solution of calcium or zinc lactate deposits its excess

of salt only gradually on cooling. Finely powdered calcium lactate induces the solidification of a supersaturated solution of calcium lactate in two hours, whilst glass powder, lycopodium, or cotton filaments do not effect the change till the following day. The solution deposits its excess of salt some hours sooner when exposed to air than when contained in sealed tubes, but in both cases the excess separates sooner or later.

At 10°, 1 part of zinc lactate requires for solution about 90 parts of water. C. G. S.

Conversion of Dextrotartaric into Racemic Acid.

By E. JUNGFLEISCH (Compt. rend., lxxv, 439—443).

THIRTY grams of dextrotartaric acid, with three or four grams of water, heated in sealed tubes to 175° for 30 hours, formed some insoluble black matter, together with a coloured syrupy liquid, which gradually deposited acicular crystals in abundance, and gave off a considerable quantity of gas. The contents of the tubes were boiled with water, and the filtrate was evaporated on a water-bath, whereupon it deposited crystals of racemic acid, which, by a second crystallisation, were obtained pure and white. The mother-liquors, by evaporation to a syrup and re-heating, furnished a fresh crop of racemic acid.

If the temperature during the heating of the sealed tubes, be raised above 175°, the tubes are liable to burst; if it be below 175°, the reaction is sluggish. The racemic acid is found to be identical with that obtained from the tartar of certain wines. The same reaction takes place without the presence of water, but the product is small in quantity.

In another experiment 650 grams of tartaric acid and 100 grams of water, heated in an enamelled steel vessel for 48 hours to 180°, gave several hundred grams of racemic acid. The gas formed was allowed to escape two or three times during the process.

C. G. S.

Quercite-Sulphuric Acid and a Sugar derived therefrom and different from Quercite. By C. SCHEIBLER (Deut. Chem. Ges. Ber., v, 845).

FINELY powdered quercite dissolves without evolution of gas in sulphuric acid heated on the water-bath, no coloration being produced; the acid liquid neutralised with barium carbonate, furnishes the non-crystalline barium salt of *quercite-sulphuric acid*; from this the acid is obtainable by decomposition with sulphuric acid; it is a syrupy mass, and yields varnish-like calcium, zinc, cadmium, and copper-salts. The barium-salt, heated with water in a tube to 120°—125°, decomposes, furnishing barium sulphate, sulphuric acid, and a new sugar, which crystallises easily, and is not identical with the original quercite.

C. R. A. W.

Pentachlorobenzene. By A. LADENBURG (Deut. Chem. Ges. Ber., v, 789—790).

JUNGFLEISCH, as well as Otto, state that this compound exists in two isomeric modifications, but according to Kekulé's theory, which is now

generally accepted, only one pentachlorobenzene can exist. On repeating Jungfleisch's experiments, the author could only obtain the following compounds:—

	Boiling-point.	Melting-point.
$C_6Cl_4H_2$..........	245°—248°	27°—28°
C_6Cl_5H..........	275°—277°	85°—86°
C_6Cl_6............	—	235°

These bodies were produced by acting with *moist* chlorine upon chlorobenzene, treating the product with alcoholic potash, and separating the different compounds by repeated fractional distillation, recrystallisation, &c.

From these results it appears that by acting with moist chlorine upon chlorobenzene in the sunlight, only one pentachlorobenzene is formed. The existence of another modification is very doubtful, for the statements of Jungfleisch and Otto do not agree, and according to the former this isomeride has a melting point varying between 175° —198°. Moreover all the compounds which Jungfleisch obtained by using *dry* chlorine are also formed by the moist gas with the exception of this isomeride.*

C. S.

Dinitrobromobenzene and Phenylenediamine. By TH. ZINCKE and F. SINTENIS (Deut. Chem. Ges. Ber., v, 791—795).

WALKER and Zincke have shown that the two nitrobromobenzenes which are formed by the nitration of bromobenzene yield, by the further action of nitric acid, one and the same dinitro-bromobenzene, melting at 72°. If the bromine occupies the position 1, the side-chains in the two nitrobromobenzes are 1 : 2 and 1 : 3, and consequently in dinitrobromobenzene they must be either 1 : 2 : 3, or 1 : 3 : 6 (supposing that 1 : 2 is identical with 1 : 6).

To decide this question, dinitrobromobenzene was reduced by means of tin and hydrochloric acid; the bromine was eliminated by the nascent hydrogen and *paraphenylenediamine* was formed, showing that in dinitrobromobenzene the side-chains occupy the positions 1 : 3 : 6.

C. S.

Chlorinated Azo-Derivatives of Benzene. By K. HEUMANN (Deut. Chem. Ges. Ber., v, 910—915).

WHEN solid (α) chloronitrobenzene is heated with alcoholic potash, a violent reaction takes place, and the mixture on cooling solidifies to a mass of long hair-like crystals, consisting of *dichlorazoxybenzene*, $C_6H_4Cl\underbrace{N-N}_{O}ClH_4C_6$. This compound melts at 155°—156°, is insoluble

* In a recent note (*Bull. Soc. Chim.*, Dec. 1872, p. 531), Jungfleisch maintains the existence of the second pentachlorobenzene described by himself and by Otto, and attributes Ladenburg's failure in obtaining it to the fact of his having used moist instead of dry chlorine. He also declares his intention of publishing further results relating to the second pentachlorobenzene and its derivatives.

in water, and sparingly soluble in alcohol, from which it is deposited in pale yellow needles having a silky lustre.

The fluid (β) modification of chloronitrobenzene, when treated with alcoholic potash, yielded a small quantity of dichlorazoxybenzene identical with that above described; the action was, however, less energetic than that produced by alcoholic potash on the solid modification of chloronitrobenzene, and there still remained portions of the fluid chloronitrobenzene unacted on, although an excess of potash was employed. Hence the author surmises that the fluid modification of chloronitrobenzene does not yield dichlorazoxybenzene, and that the formation of that substance arose from the presence of a small proportion of the solid chloronitrobenzene in the fluid chloronitrobenzene employed.

When chlorazoxybenzene is dropped into warm fuming nitric acid, it is dissolved, and the solution, on addition of water, or on cooling, deposits a bright yellow nitro-compound, which was found to be *dichloromononitroazoxybenzene*, $C_6H_3Cl(NO_2)\underset{\diagdown O \diagup}{N—N}ClH_4Cl_6$. It melts at 134°, is insoluble in water, and sparingly soluble in alcohol, from which it is deposited in felt-like flocks, consisting of small needles. Its crystals possess a beautiful silky lustre, and are difficult to powder. It appears to be reduced by ammonium sulphide, but the product was not isolated.

Dichlorazoxybenzene added to fuming sulphuric acid dissolves with slight evolution of heat, the solution at the same time acquiring a metallic reflex, like that of the aniline colours, and on cooling a crystalline substance is deposited, which, when boiled with alcohol and animal charcoal, yields long, reddish-yellow needles having the composition of *dichlorazobenzene*. This substance melts at 183°, is insoluble in water, and sparingly soluble in alcohol. Apparently dichlorazobenzene is not the sole product of this reaction.

If solid chloronitrobenzene be heated with alcoholic potash, and, after the conversion into dichlorazoxybenzene, the mixture be distilled in a retort, a stage is reached at which a violent reaction takes place, a yellowish-red sublimate and oily drops passing over. The oily drops proved to be chloraniline, melting at 64°, while the crystalline sublimate was found to be dichlorazobenzene, melting at 183°, and identical with that described above. By the action of nascent ammonium sulphide on dichlorazobenzene, the author has obtained white needles, which he is still investigating; he is also engaged in extending his researches to the bromonitro-benzenes, and to the corresponding toluene derivatives.

T. B.

Action of Sodium on Chlorinated Nitro-compounds. By A. W. Hofmann and Geyger (Deut. Chem. Ges. Ber., v, 915—919).

Chloronitrobenzene, melting at 83°, was dissolved in anhydrous ether, and small fragments of sodium were added. Under these circumstances the metal was found to be gradually transformed into a black, friable

substance, which, on exposure to the air, became warm and turned yellow. Placed in water it dissolved with a red colour, and when heated to 100° with ether and methyl iodide, it yielded a yellow, crystalline mass, which, on distillation with water, gave a distillate containing methyl iodide and chloronitrobenzene melting at 83°, while the residue when crystallised from alcohol yielded dichlorazoxybenzene. The black substance, when treated with concentrated hydrochloric acid, yielded a yellow crystalline mass similar to that obtained by the action of methyl iodide, and like it yielding dichlorazoxybenzene.

When the black substance was suspended in ether and treated with benzoyl chloride, an energetic action took place, the black colour changing to yellow. The product, on being distilled with water, gave a distillate containing nitrochlorobenzene, while the residue, on crystallisation from alcohol yielded a substance having the composition, $C_{26}H_{18}N_2Cl_2O_3$, and crystallising in long prisms. It melts at 125°, is insoluble in water, and tolerably soluble in alcohol or ether. This substance may be regarded as hydrochlorazoxybenzene, in which two hydrogen-atoms are replaced by benzoyl—

$$\begin{array}{ccc} C_6H_4ClN & —O— & NClH_4C_6 \\ | & & | \\ C_7H_5O & & C_7H_5O. \end{array}$$

The black substance may be regarded as containing the corresponding sodium compound—

$$\begin{array}{ccc} C_6H_4ClN & —O— & NClH_4C_6 \\ | & & | \\ Na. & & Na. \end{array}$$

With the view of obtaining the analogous hydrogen-compound the authors heated dichlorazoxybenzene with alcoholic ammonium sulphide. The result, however, was a substance crystallising from alcohol in beautiful colourless crystals and melting at 122°. Analysis showed that the oxygen of the dichlorazoxybenzene had been eliminated, two atoms of hydrogen being fixed at the same time. The substance is therefore *hydro-dichlorazobenzene*. When its alcoholic solution is boiled in the air for a long time, or heated to the boiling point in contact with animal charcoal, the liquid becomes yellow and deposits crystals of dichlorazobenzene.

Sodium has no action on an ethereal solution of fluid chloronitrobenzene, but bromonitrobenzene, melting at 126°, when dissolved in ether and treated with sodium, yielded a black substance, which, when decomposed by ethyl iodide or hydrochloric acid, gave *dibromazoxybenzene*, $C_{12}H_8Br_2N_2O$, a substance crystallising from alcohol in leaflets and melting at 172°.

Chloronitrotoluene when similarly treated with sodium yielded a black substance, which was converted by hydrochloric acid into *dichlorazoxytoluene*, $C_{14}H_{12}Cl_2N_2O$. This substance forms small felted needles insoluble in water, slightly soluble in alcohol, easily soluble in ether, and melting at 128°.

It is worthy of note that attempts to form an analogous compound by the action of sodium on nitrobenzene did not succeed. This con-

firms the observation that bodies derived from benzene by the replacement of several hydrogen-atoms differ notably from those benzene derivatives in which only one hydrogen atom is replaced.

T. B.

Some Derivatives of Diphenylmethane. By W. H. Doer (Deut. Chem. Ges. Ber., v, 795—797).

Dinitro-diphenylmethane, $C_{13}H_{10}(NO_2)_2$, is produced by dissolving the hydrocarbon in cold, fuming nitric acid of specific gravity 1·5° It is insoluble in water and alcohol, sparingly soluble in ether, and crystallises from hot benzene in long, brittle, iridescent needles, melting at 183°.

Isodinitro-diphenylmethane, $C_{13}H_{10}(NO_2)_2$, is formed when diphenylmethane is heated on a water-bath with nitric acid of specific gravity 1·4. It is insoluble in water, but soluble in alcohol, ether, benzene, and acetic acid, and crystallises in small straw-coloured needles, showing a blue lustre and melting at 172°.

Tetranitro-diphenylmethane, $C_{13}H_8(NO_2)_4$, is the chief product formed by the action of a well-cooled mixture of concentrated nitric and sulphuric acid on diphenylmethane. It is insoluble in water, alcohol, and ether, sparingly soluble in benzene, a little more in glacial acetic acid, from which it crystallises in brilliant, pale-yellow, hard prisms, melting at 172°.

Diamido-diphenylmethane, $C_{13}H_{10}(NH_2)_2$, crystallises from alcohol in small pearly scales, melting at 85° and having the greatest resemblance to benzidine. The hydrochloride is very soluble in water and alcohol, and crystallises from dilute hydrochloric acid in small white plates. The sulphate is sparingly soluble in alcohol, and crystallises from water in small brilliant plates.

Isodiamido-diphenylmethane and its salts are very unstable compounds which could not be obtained in a pure state.

Diphenylmethane-disulphonic acid is formed by dissolving the hydrocarbon in an excess of fuming sulphuric acid on a water-bath. The potassium salt, $C_{13}H_{10}(SO_3K)_2 + H_2O$, crystallises from dilute alcohol in small shining prisms. The barium salt is anhydrous, and crystallises from an aqueous solution in very small scales. The copper salt, $C_{13}H_{10}(SO_3)_2Cu$, is soluble in water and crystallises from dilute alcohol in small, green shining plates. The free acid, $C_{13}H_{10}(SO_3H)_2$, is obtained from an aqueous solution in small deliquescent plates and from alcohol in arborescent needles, melting at 59°.

Bromine acts violently on diphenylmethane, forming a viscid substance, which, after standing for months, yields crystalline crusts forming large tables when re-crystallised from ether. This body contains 4 atoms of bromine, but the quantity was not sufficient to decide whether it is an addition- or a substitution-product.

Dinitro-benzophenone, $C_{13}H_8O(NO_2)_2$, is formed by boiling dinitro-diphenylmethane with a chromic acid solution; it is also obtained by the nitration of benzophenone, and is identical with that which Linnemann obtained by the action of nitric acid on benzhydrol. It crystallises from a mixture of alcohol and ether in small, shining needles, melting at 129·5°.

Isodinitro-benzophenone is not produced in the nitration of benzophenone, but is formed by oxidising isodinitro-diphenylmethane. It is soluble in alcohol, ether, benzene, and acetic acid. From alcohol it crystallises in short straw-coloured needles or pale-yellow prisms; it melts at 118°.

Diamido-benzophenone is identical with Laurent's and Chancel's *flavine*: it forms long, pale-yellow needles, melting at 165°. The corresponding iso-compound could not be obtained in the pure state.

C. S.

Triphenylmethane. By A. Kekulé and A. Franchimont (Deut. Chem. Ges. Ber., v, 906—908).

Triphenylmethane, $CH(C_6H_5)_3$, is obtained by heating one molecule of benzylene dichloride with two molecules of mercury-diphenyl:—

$$C_6H_5.CHCl_2 + 2(C_6H_5)_2Hg = CH(C_6H_5)_3 + 2C_6H_5HgCl.$$

It is a solid, melting at 92·5°, and boiling at about 335°. From an alcoholic solution it separates in brilliant, well-formed crystals; it is also readily soluble in ether and benzene, forming with the latter hydrocarbon the compound $CH(C_6H_5)_3.C_6H_6$. This compound forms large transparent crystals, which melt at 76°, and at this temperature or when exposed to the air, give off the benzene and become white and opaque. Triphenylmethane is also soluble in toluene, but does not combine with it. On dissolving it in warm fuming sulphuric acid, it is converted into the sulpho-acid, $CH(C_6H_4.SO_3H)_3$, the barium salt of which is precipitated by alcohol from an aqueous solution in fine white needles. No other salt could be obtained crystallised, but a concentrated solution of the free acid solidifies on standing to a crystalline mass.

C. S.

On Benzophenone-chloride and the Formation of Anthraquinone in the Preparation of Benzophenone. By A. Kekulé and A. Franchimont.

The authors prepared pure *benzophenone-chloride* or *diphenyldichloromethane*, $CCl_2(C_6H_5)_2$, with the object of obtaining tetraphenylmethane by acting on it with mercury-diphenyl.

According to Behr (*Deut. Chem. Ges. Ber.*, iii, 752), this chloride cannot be obtained in the pure state, because it is decomposed by distillation; but this is not quite correct. By heating benzophenone with phosphorus pentachloride for an hour or two in a flask connected with a reversed condenser, and distilling the product under a diminished pressure in a weak current of air, pure diphenyl-dichloromethane is obtained. It boils constantly at 220° under a pressure of 671 mm., and is a colourless, very refractive liquid, which is acted on by water slowly in the cold, quickly when heated, with formation of benzophe-

none and hydrochloric acid. Under the common pressure it boils with slight decomposition at 305°.

The benzophenone used in these experiments was obtained by distillation of calcium benzoate. Besides the ketone, other bodies were formed in small quantity, amongst which there was some *anthraquinone* and a body crystallising from benzene in brilliant prisms, melting at 145°, and having, according to one analysis, the formula $C_{14}H_{10}$. The formation of the quinone may be explained by the equation:—

$$2C_7H_6O_2 - 2H_2O = C_{14}H_8O_2.$$

C. S.

Phenoquinone and similar Compounds. By H. WICHELHAUS (Deut. Chem. Ges. Ber., v, 846).

THE oxidation of phenol gives rise to phenoquinone, $C_{18}H_{14}O_4 = C_6H_4\left\{\begin{matrix}O.O.C_6H_5\\O.O.C_6H_5\end{matrix}\right.$; this substance is the prototype of a number of compounds.

Pyrogallic acid solution dissolves quinone and produces a red crystalline product, which does not melt below 200°, and can be sublimed but not without considerable loss. The reaction is:—

$$\underset{\text{Quinone.}}{2C_6H_4O_2} + \underset{\text{Pyrogallic acid.}}{2C_6H_6O_3} = \underset{\text{Hydroquinone.}}{C_6H_6O_2} + \underset{\text{Pyrogalloquinone.}}{C_6H_4\left\{\begin{matrix}O.O.C_6H_3(OH)_2\\O.O.C_6H_3(OH)_2.\end{matrix}\right.}$$

This substance, *pyrogalloquinone*, is decomposed by alkalis, forming blue solutions which soon become black.

By oxidation with chromic acid solutions pyrogallic acid forms a product difficultly soluble in chloroform and benzene, crystallisable with some difficulty from hot alcohol; this substance is probably identical with the *purpurogallin* of Aimé Girard, obtained by oxidising pyrogallic acid with sulphuric acid and potassium permanganate; the author, however, deduces the formula—

$$C_{18}H_{14}O_9 = C_6H_3\left\{\begin{matrix}OH\\O.O.C_6H_3(OH)_2\\O.O.C_6H_3(OH)_2.\end{matrix}\right.$$

whereas Girard considered his product to be $C_{20}H_{16}O_9$.

The author views *quinhydrone* as $C_{18}H_{14}O_6 = C_6H_4\left\{\begin{matrix}O.O.C_6H_4(OH)\\O\,O.C_6H_4(OH)\end{matrix}\right.$, *i e.*, as a body belonging to the class of substances under consideration. Wohler's analytical numbers agree well with this formula; the body has, however, been usually regarded as $C_{12}H_{10}O_4$.

All the phenols of the aromatic series (cresol, thymol, resorcin, α-naphthol, β-naphthol, &c.) react with quinone in a similar way; thymoquinone also reacts thus, but the difficultly reducible anthraquinone does not undergo such changes. Chloroquinone and thiophenol do not develop substitution-products in this manner; trichlorinated quinone is reduced and the chlorine removed by the action of pyrogallic acid;

tetrachloroquinone, on the other hand does not lose any chlorine, but forms tetrachloro-hydroquinone; thiophenol reduces the quinone to quinhydrone, and finally to hydroquinone.

Phenoquinone treated with aniline furnishes a crystalline product, thus—

$$C_6H_4O_2(OC_6H_5)_2 + 2(C_6H_5.NH_2) = 2(C_6H_5.OH) + C_6H_4O_2(NH.C_6H_5)_2.$$

This body is identical with the *quinone anilide* of Hofmann, who obtained it by the action of quinone on aniline, and considered it to be $C_{18}H_{14}O_2N_2$, whilst the author assigns to it the above formula = $C_{18}H_{16}O_2N_2$.

The author views the "subhydrate of nitric acid," $N_4H_2O_{11}$, recently described by Weber, as a body belonging to the same class of substances as those above described:—

$$\begin{array}{l} N\left\{\begin{array}{c}O.O\\O.O\end{array}\right\}N.OH \\ | \\ O \\ | \\ N\left\{\begin{array}{c}O.O\\O.O\end{array}\right\}N.OH \end{array}$$

C. R. A. W.

Nitrophenolsulphonic Acid. By JULIUS POST.

(Deut. Chem. Ges. Ber., v, 852—854).

THE author has converted orthonitrophenol (m.p. 110°) into the sulpho-acid by the action of fuming sulphuric acid. On adding the phenol little by little to the acid, the crystals dissolve with slight evolution of heat; the mixture is allowed to stand for some time in a cool place, and then poured into water. The warmer the mixture becomes, however, and the longer it stands, the greater is the amount of decomposition, evidenced by the evolution of sulphurous acid, and the less the yield of sulpho-acid. The author notes also that hydrocyanic is formed, in fact that it is a product of the action of fuming sulphuric acid on the nitro-derivatives of benzene and phenol generally.

The calcium salt, $\left.\begin{array}{r}C_6H_3(NO_2)O\\SO_3\end{array}\right\}Ca + 2\frac{1}{2}$ aq., crystallises in short, yellow, pliable needles, which become brick-red on heating, but regain the original colour on cooling; when dry, it may be heated to 270° without suffering decomposition. It is difficultly soluble in cold, but more soluble in hot water. The corresponding barium salt contains one molecule of water; it forms a very difficultly soluble, yellow glistening powder, which under the microscope is seen to consist of small needles.

H. E. A.

Reduction-products of Nitracetamide Compounds. By F. HOBRECKER (Deut. Chem. Ges. Ber., v, 920—924).

THE reduction is effected by treatment with tin and hydrochloric acid. Nitracetamidobenzene thus treated yields only diamidobenzene hydrochloride in almost the theoretical quantity.

Ethenyl-diamidotoluene or *Ethenyl-toluylene-diamine*. The hydrochloride is obtained by reducing nitracetamidotoluene. It is best crystallised from concentrated hydrochloric acid, and then forms warty masses. It is extremely soluble in water, soluble in alcohol, and insoluble in ether. The base is obtained by treating the hydrochloride with sodium hydrate, and crystallises in very regular rhombic plates, slightly soluble in cold water, and readily soluble in hot water, in alcohol, and in ether, melting at 203°, and volatilising without decomposition at a temperature above the boiling point of mercury. It is also unchanged by exposure to the air. Its platinum salt can be obtained from its concentrated solutions and recrystallised from dilute hydrochloric acid.

In its composition this base is strictly analogous to Hofmann's bases obtained by treating amidobenzene and its homologues with a mixture of acid and phosphorus trichloride, so that it may be also described by the second name given to it above.

Ethenyl-diamido-xylene or *Ethenyl-xylylenediamine* is obtained from nitracetamidoxylene. The hydrochloride takes the form of beautiful large concentrically-grouped needles, and is purified by crystallisation from dilute hydrochloric acid. It is readily soluble in water, less so in alcohol and dilute acids. The base separates in the solid state when the hydrochloride is treated with sodium hydrate. It is insoluble in water, readily soluble in alcohol and ether; boils without decomposition at a temperature considerably above the boiling point of mercury, and solidifies again on cooling to a transparent, friable resinoid mass, and has not been obtained in the crystalline state. Its platinum salt is obtained in beautiful needles from tolerably concentrated solutions. Its nitrate is nearly insoluble.

Ethenyl-diamidoxylene-urethane or *Ethenyl-xylylenediamine-urethane* is readily obtained by the action of chlorocarbonic ether upon the ethereal solution of the base. Its hydrochloride is quite insoluble in water, and soluble in alcohol and ether. Its crystals melt to an oily liquid in boiling water.

Ethenyl-triamidobenzene. Unlike amidobenzene, diamidobenzene acetylated, nitrated and then reduced, yields an ethenylated compound. Ethenyl-triamidobenzene forms long white needles, unchanged in the air, readily soluble in hot and cold water, and in alcohol. Its hydrochloride is crystalline and very soluble. Its nitrate is difficultly soluble. The mother-liquor from the ethenyl-triamidobenzene yields small crystals which are apparently tetramidobenzene.

E. D.

On Nitronaphthalenes. By A. de Aguiar (Deut. Chem. Ges. Ber., v, 897—906).

When pure α-dinitronaphthalene melting at 216° is gently boiled for eight hours with a large quantity of fuming nitric acid, by far the greater portion is converted into a trinitronaphthalene melting at 122°, the other products consisting of a small quantity of tetranitronaphthalene, and a somewhat larger quantity of *nitrophthalic acid*,

$C_6H_3(NO_2)(CO_2H)_2$. This acid crystallises from glacial acetic acid in beautiful white clinorhombic crystals,* melting at 212°. It is but sparingly soluble in cold water, a little more freely in boiling water, and in almost every proportion in alcohol, forming a yellowish solution. By sublimation it can be obtained in feathery crystals, but it detonates when quickly heated. This acid appears to be identical with that obtained by Marignac (Gerhardt, vol. iii, 485).

Barium nitrophthalate, $C_6H_3(NO_2)(CO_2)_2Ba$, crystallises when a hot aqueous solution of the acid is nearly saturated with barium carbonate, in brilliant, yellowish, microscopic plates, which are very sparingly soluble in cold and hot water. *Silver nitrophthalate*, $C_6H_3(NO_2)(CO_2Ag)_2$, is a heavy, white precipitate, which explodes when heated.

Beilstein, by heating α-dinitronaphthalene with a mixture of fuming nitric acid and sulphuric acid, obtained a trinitronaphthalene melting at 147°. This isomeride is also formed when dinitronaphthalene is boiled with nitric acid for several days, and can be easily obtained perfectly pure by adding 150 grams of concentrated sulphuric acid to a mixture of 150 grams of fuming nitric acid and 9 grams of dinitronaphthalene, diluting the clear solution with water, and recrystallising the precipitate from chloroform. The *pure* compound melts at 154°.

When β-dinitronaphthalene, melting at 170°, is boiled with nitric acid for eight hours, it yields β-trinitronaphthalene, melting at 218°, β-tetranitronaphthalene, melting at 200°, and a nitrophthalic acid, which is different from that from α-dinitronaphthalene.

The best method of preparing pure β-trinitronaphthalene consists in adding 50 grams of sulphuric acid to a mixture of 50 grams of fuming nitric acid and 10 grams of β-dinitronaphthalene, and crystallising the product from glacial acetic acid.

C. S.

A new Hydrocarbon isomeric with Anthracene. By C. GRAEBE (Deut. Chem. Ges. Ber., v, 861—862).

THE author states that numerous attempts to isolate the hydrocarbons which occur in crude anthracene together with anthracene and acenaphthene were unsuccessful. Dr. Glaser, working on the large scale, however, has been able to separate one of these accompanying hydrocarbons, and has submitted it to the author for examination. After a single recrystallisation it was so pure that the melting point was not altered by continuing the purification. Analysis and vapour-density determination lead to the formula $C_{14}H_{10}$, which is confirmed by the examination of its derivatives.

The new hydrocarbon resembles anthracene in many respects, but differs remarkably in others; it crystallises in plates, and exhibits a blue fluorescence. It melts at 105°, and boils at 340° (thermometer wholly immersed in the vapour). It is slightly soluble in cold, more soluble in hot alcohol; benzene, ether, and carbon disulphide dissolve it readily.

It unites with trinitrophenol to form $C_{14}H_{10}.C_6H_2(NO_2)_3OH$, which

* The drawings and measurements of these crystals are given in the original paper.

crystallises in reddish-yellow needles melting at 144°. It is less readily oxidised than anthracene, but is converted by chromic acid into the quinone, $C_{14}H_8O_2$, which crystallises from benzene in yellow needles, darker than those of anthraquinone, melting at 205°. This quinone does not yield nitro-derivatives when heated with concentrated nitric acid, but is converted into the dinitro-quinone, $C_{14}H_6O_2(NO_2)_2$, by a mixture of concentrated nitric and sulphuric acid. Acted upon by concentrated sulphuric acid under conditions which in the case of anthraquinone give rise to the formation of sulpho-acids, it is for the greater part carbonised; and whereas anthraquinone dissolves on reduction by zinc-dust and soda, with production of a beautiful red colour, the new quinone yields at first a green solution, which afterwards becomes dirty red.

The new hydrocarbon differs also from anthracene in its behaviour with nitric acid (1·4), in which it dissolves, with evolution of heat, forming a yellow crystalline mononitro derivative.

Sulphuric acid at 100° converts the new hydrocarbon, without the least carbonisation, into a monosulpho-acid.

H. E. A.

A New Hydrocarbon isomeric with Anthracene.

By Ernst Schmidt (Deut. Chem. Ges. Ber., v, 930—932).

On nitration of anthracene by Bolley's method, in alcoholic solution, a mixture of isomeric mononitro-derivatives is obtained, consisting of a red and a white mononitro-anthracene.

If the former be acted upon by tin and hydrochloric acid, the red body disappears after a time, and is replaced by a yellowish-grey substance, readily purified by recrystallisation from alcohol or benzene. The same compound is formed in small quantity on subliming red mononitroanthracene, together with a yellow substance (possibly dinitroanthracene) of lower melting point.

The new body has the composition $C_{14}H_{10}$, being isomeric with anthracene and also with Graebe's isomeride; it crystallises in thin silky, glistening plates, which exhibit a violet-blue fluorescence; it melts at 247°. It is almost insoluble in cold, but more soluble in hot alcohol; benzene, chloroform, and carbon disulphide dissolve it readily. It unites with trinitrophenol, forming a compound crystallising in reddish-yellow needles.

It is not affected, even by prolonged heating, with nitric acid of sp. gr. 1·2, but is readily acted upon by more concentrated or fuming acid. Sulphuric acid at 100° has no action, but on further heating dissolves the hydrocarbon, and converts it into a sulpho-acid, forming a bluish-green solution, without the least carbonisation.

Amidanthracene is also formed, together with the new hydrocarbon.

The author promises further communications on this remarkable reaction, and on the nitration products of anthracene and its substitution derivatives.

H. E. A.

A new Hydrocarbon from Coal-tar Oil. By E. OSTERMAYER and R. FITTIG (Deut. Chem. Ges. Ber. v, 933—936).

AT the "Naturforscherversammlung" at Leipzig in August last, Prof. Fittig brought forward a communication on the above subject, and exhibited a number of highly characteristic and well crystallised derivatives of the new hydrocarbon. He stated that the analyses led to the formula $C_{16}H_{12}$, but at the same time expressly drew attention to the fact, that the whole behaviour of the hydrocarbon was rather in accordance with the view that it was an isomeride of anthracene, which indeed subsequent experiments have shown is the case.

The hydrocarbon was obtained from the liquid portion of coal-tar oil boiling above 300° by fractional distillation, refrigeration of the middle distillates, pressing the crystalline mass, and repeated recrystallisation from alcohol. The melting-point lay between 97° and 99°. The mean of three analyses gave 93·58 per cent. of carbon and 6·05 per cent. of hydrogen. The formula $C_{16}H_{12}$ requires 94·11 per cent. of carbon and 5·89 of hydrogen, whilst the formula $C_{14}H_{10}$ requires 94·38 of carbon and 5·62 of hydrogen.

It gave a compound with trinitrophenol crystallising in small red needles, and consisting of equal numbers of molecules of the constituents.

On heating an ethereal solution of the hydrocarbon with bromine, the additive compound $C_{14}H_{10}Br_2$, was obtained, which forms colourless four-sided prisms. This decomposes spontaneously on keeping. Alcoholic potash easily removes all the bromine from it, and apparently regenerates the hydrocarbon.

If 1 part of the hydrocarbon is warmed with a mixture of 1 part of potassium dichromate and $1\frac{1}{2}$ part of sulphuric acid, previously diluted with thrice its volume of water, an energetic reaction takes place, carbonic anhydride is evolved, and an orange-yellow mass is produced, consisting of the quinone $C_{14}H_8O_2$. This crystallises in magnificent orange-yellow long needles, melting at 198°. It is converted, by heating with sulphurous acid solution, into colourless glistening needles of a highly unstable hydro-derivative. It is reduced by zinc-dust with much greater difficulty than anthraquinone, but yields the original hydrocarbon convertible into the same quinone Analysis of the regenerated hydrocarbon gave 94·05 per cent. of carbon and 5·75 per cent. of hydrogen.

Anthraquinone may be heated for a day with the above oxidising mixture without undergoing alteration; the new quinone, however, is readily oxidised to a well characterised bibasic acid of the composition $C_{14}H_{10}O_4 = \begin{cases} C_6H_4.COOH \\ C_6H_4.COOH \end{cases}$, which the authors term *diphenic acid*.

Heated with an excess of lime, the new acid is converted into the compound $C_{13}H_8O$ thus:—

$$\begin{cases} C_6H_4.COOH \\ C_6H_4.COOH \end{cases} = \begin{Bmatrix} C_6H_4 \\ C_6H_4 \end{Bmatrix} CO + CO_2 + H_2O.$$

This *diphenylene ketone* is converted by fusion with potassium hydrate into the potassium salt of *diphenylmonocarbonic* acid, thus—

$$\left\{\begin{matrix} C_6H_4 \\ C_6H_4 \end{matrix}\right\} CO + KOH = \left\{\begin{matrix} C_6H_4.COOK \\ C_6H_5. \end{matrix}\right.$$

In conclusion the authors state that the above derivatives show that the constitution assigned by Graebe and Liebermann (this *Journal*, x, 444) to ordinary anthracene really belongs to the new isomeride, and that the constitution of ordinary anthracene is therefore probably expressed by Graebe and Liebermann's second formula (*Ann. Chem. Pharm.*, *Supplement*, vii, 315).

H. E. A.

Derivatives of Uramidodracylic Acid. By PETER GRIESS (Deut. Chem. Ges. Ber., v, 855—857).

A SINGLE *dinitro-uramidodracylic* acid is produced by the action of strong nitric acid on uramidodracylic acid; it forms small, yellow-white, indistinct plates or prisms, almost insoluble in cold water and also in cold alcohol and ether.

Heated with water it is converted into *nitroamidodracylic* acid:—

$$C_8H_6N_4O_7 = C_7H_6N_2O_4 + CO_2 + N_2O.$$

which crystallises in small intensely yellow needles, difficultly soluble, even in boiling water. The barium and silver salts are described. Nitroamidodracylic acid is the fourth acid of the composition $C_7H_4(NO_2)(NH_2)O_2$, being *isomeric* with α, β, and γ nitroamidobenzoic acids from uramidobenzoic acid (this *Journal*, x, 497); it is converted, however, by the action of nascent hydrogen into a *diamidobenzoic* acid, *identical* with the reduction product of the above mentioned β-nitroamidobenzoic acid, and yielding diamidobenzene (melting-point 99°) on distillation.

By heating nitroamido-dracylic and β-nitroamidobenzoic acids with potash, they are converted into *nitro-oxy* acids, according to the equation:—

$$C_7H_4(NO_2)(NH_2)O_2 + H_2O = C_7H_4(NO_2)(OH)O_2 + NH_3,$$

but the two products are *isomeric*.

Oxynitrodracylic acid crystallises in whitish-yellow needles, which separate almost entirely from a hot aqueous solution on cooling. It melts at 185°.

β-oxynitrobenzoic acid crystallises in long yellow four- or six-sided plates, even less soluble in water than the isomeride, and melts at 230°. It yields a highly characteristic barium salt, on the addition of barium chloride to its ammoniacal solution, in the form of magnificent yellow-red glistening plates, of the composition $C_7H_3(NO_2)O_3,Ba$ + aq., almost insoluble in water. These two acids differ, moreover, both from nitrosalicylic acid and from Gerland's oxynitrobenzoic acid.

H. E. A.

The Chemical relation of Phosphorus to Turpentine Oil, and the action of the latter as an Antidote in Phosphorus Poisoning. By KOHLER and SCHIMPF (Chem. Centr., 1872, 294).

IF $\frac{3}{4}$ of an ounce of phosphorus be gradually added to 2 lbs. ordinary turpentine oil warmed to 40°, and the mixture be shaken on the sand-bath, there crystallises out, on cooling, a crystalline white solid, which is separated from excess of phosphorus by crystallisation from alcohol. This substance has an acid reaction. On exposure to the air it becomes changed into a resinous substance, smelling like pine oil, in which phosphoric acid may be detected. At 40° this substance is decomposed in a stream of hydrogen, inflammable phosphoretted hydrogen being evolved; above 50° it is decomposed into a resinous mass.

The baryta salt of this new acid—called by the author *turpentine phosphoric acid*—has the formula $C_{20}H_{15}PO_3Ba$.

Turpentine oil, when administered as an antidote in phosphorus poisoning, forms this compound with the phosphorus, in which form it is discharged in the urine, and is found in the alkaline distillate when the urine is distilled. This distillate reduces mercuric to mercurous chloride, and precipitates metallic silver from solutions of its salts.

These reactions apply only to ordinary turpentine oil containing oxygen. The relations of the chemically pure oil to phosphorous are being investigated by the authors.

M. M. P. M.

The Presence of an Organic Alkali in Boldo.
By E. BOURGOIN and C. VERNE (Pharm. J. Trans. [3], iii, 323).

THE boldo is a tree indigenous to Chili, and belongs to the order *Monimiaceæ*. It is the *Boldoa fragrans* of Jussieu, the *Ruizia fragrans* of Ruiz and Pavon, and the *Peumus fragrans* of Persoz. Baillon has recently described it under the name of *Peumus boldus*. The leaves contain an essential oil and an alkaloïd.

The latter, which does not appear to be crystallisable, is very slightly soluble in water, to which, however, it communicates an alkaline reaction and bitter taste. It is soluble in alcohol, ether, chloroform, caustic alkalies, and benzene. From solution in acids it is precipitated by ammonia and by the double iodide of mercury and potassium, and gives with solution of iodine a chestnut-brown precipitate. Concentrated nitric acid immediately colours it red, and it assumes the same coloration in the cold with sulphuric acid.

W. A. T.

Solvents for Indigo. By E. JACOBSEN (Chem. News, xxvi, 234).

IN addition to the solvents for indigo mentioned by de Aguiar, Baeyer, and Wartha, the following substances will dissolve it, in greater or less quantity, at their boiling-points:—Nitrobenzene, castor-oil, acetone, chloral hydrate, camphor, oil of turpentine, balsam of copaiba, cedar oil, amylic alcohol, oil of lavender, white bees-wax, Japanese

vegetable wax, and Carnauba wax (from this last small flaky crystals separate).

A solution of indigo in white wax, when heated for some time at its boiling point, passes through several shades of colour, and finally becomes brown, owing to the reduction of the indigo. When powdered indigo is added to melting picric acid, deflagration takes place.

J. W.

Physiological Chemistry.

New Researches on the Coagulation of Fibrin. By ALEXANDER SCHMIDT (Pflüger's Archiv., vi, 413—490, and 491—538).

THE author retains the name of fibrinoplastic substance for the albuminous body which he formerly described under that title, and which Kühne subsequently called paraglobulin, and maintains that it is quite distinct from serum-albumin, in opposition to Brücke, who considered them identical, and gave the name of fibrinoplastic substance to an unknown body. Fibrinoplastic substance is completely precipitated when its alkaline solutions are exactly neutralised, provided no neutral salts, or any excess of alkali, which would form a neutral salt during neutralisation, are present in the solution. If the fluid contains neutral salts the fibrinoplastic substance is not precipitated until it has been rendered acid. The quantity of acid necessary for precipitation increases proportionately to that of the salts present. The precipitate is soluble in excess of acid. As serum contains neutral salts it must be acidulated in order to precipitate the fibrinoplastic substance it contains. The quantity of acid required for the complete precipitation of 100 c.c. of ox serum is four drops of 25 per cent. acetic acid, while three drops of dilute acid are sufficient for 10 c.c. of horse serum. After the addition of the acid, the serum is to be diluted with 15 volumes of water. The amount of fibrinoplastic substance may be quantitatively determined by precipitating with dilute acid, allowing the liquid to stand from 24 to 48 hours, and then filtering. The neutralised filtrate has no fibrinoplastic action. The fibrinoplastic power of the precipitate is not impaired in the least by precipitation with acid. The quantity of fibrinoplastic substance formed by this method in 100 c.c. of ox serum is 0·72 to 0·8 grams, in a similar quantity of horse serum 0·31 to 0·56.

Fibrinoplastic substance can also be precipitated by passing carbon dioxide through the diluted serum, till a sufficient degree of acidity has been produced. The solubility of fibrinoplastic substance in caustic soda, sodium carbonate, or acetic acid is independent of the quantity of water in which it is suspended, so that a given amount of these reagents always dissolves the same quantity of fibrinoplastic substance, whether it be mixed with much or little water. Its solubility in sodium bicarbonate, sodium phosphate, and neutral alkaline salts, is in inverse ratio to the quantity of water, so that fibrinoplastic substance is precipitated from its saline solutions by addition of water, unless more salt is added

at the same time. A greater or less proportion of the fibrinoplastic substance, however, is retained in solution by the salts present, and is only thrown down by acidulation. The addition of acid alone will precipitate fibrinoplastic substance without dilution. The fibrinoplastic substance in serum is not kept in solution by neutral salts, as their quantity is insufficient, and though the alkaline hydrates, carbonates, and phosphates would suffice, yet some other solvent must be present, as serum is able, even after neutralization, to dissolve more than twice the quantity of fibrinoplastic substance it contains. This may, perhaps, be serum albumin. Fibrinoplastic substance is dissolved by oxygen passed through the water in which it is suspended; in such solutions it exhibits the same properties as in a saturated alkaline solution. It is still more soluble in carbonic acid than in oxygen, and in such a solution it exhibits fibrinoplastic properties, provided that the solution of fibrinogen added to it contains sufficient alkali to neutralise the acidity of the liquid. When this is not the case, the fluid will not coagulate till the carbonic acid has escaped. Fibrinoplastic substance is precipitated from its solution in carbonic acid by oxygen, and from its solution in oxygen by carbonic or by acetic acid, but its solution in acetic acid is not precipitated by oxygen. When freshly precipitated it forms a snow-white pulp, which, if left on the filter and covered so as to prevent it from drying, becomes converted in a few days into a yellow, sticky, syrupy mass, readily soluble in distilled water. In this condition the substance preserves all its other characters unchanged. Possibly this change is due to the absorption of oxygen. When fibrinoplastic substance is coagulated by the addition of alcohol to a concentrated solution obtained in the manner just described, it loses its fibrinoplastic properties. The author considers this to indicate that the fibrinoplastic property belongs to the albuminous substance precipitated, and not to any other substance mixed with it, as Brücke is disposed to think. The ferment of which he afterwards speaks is not affected by the alcohol.

In a former paper the author stated that the precipitate formed in a solution of fibrinoplastic substance by cupric sulphate was insoluble in excess of the reagent, while that from a solution of albumin was soluble. In this, as Brücke found, he was mistaken, and his statement that the chemical reactions of fibrinoplastic substance are unaltered by boiling its alkaline solutions, is likewise erroneous, as it is rendered insoluble in alkaline salts, though it remains soluble in dilute acids and alkalis. He considers that several of Brücke's other reasons for considering serum albumin and fibrinoplastic substance identical are vitiated by the assumption, without proof, that serum albumin is insoluble in water. The author thinks with Hoppe-Seyler, that it is soluble in water, while paraglobulin is not; but even if it be granted that serum albumin is rendered soluble by the extremely minute quantity of salts with which it is combined, its solubility is independent of the proportion of salts in the solution, and in this it differs from fibrinoplastic substance. Fibrinogen is much less easily soluble in alkalis or neutral salts than fibrinoplastic substance. It also can only be precipitated from its normal albuminous solutions, such as pericardial fluid, by acidulation and dilution, while acidulation alone suffices to precipitate it from arti-

ficial solutions in neutral salts. Another solvent must here, as in the case of fibrinoplastic substance, be present in the natural solution. As both fibrin generators are completely precipitated from their alkaline solutions by neutralisation, they produce no fibrin when neutralised either before or immediately after their admixture, while the natural solutions, containing as they do another solvent, coagulate as usual after neutralisation. An alkaline solution of fibrinoplastic substance, in which excess of alkali has been avoided, is not less active, as the author formerly thought, but more active than the same quantity of substance in its natural solution in serum. On the other hand an artificial alkaline solution of fibrinogen always coagulates slowly and incompletely. Fibrinogen is best prepared by saturating pericardial fluid with sodium chloride, completely separating the albuminous body, which, after some time, is precipitated from the mother-liquor by filtration, and then dissolving it in water. On adding to this solution solid fibrinoplastic substance prepared in a similar manner from serum by precipitation with salt, or by precipitation with acetic acid, fibrin is formed. A solution of fibrinoplastic substance in alkali, without excess, acts in the same way. The experiment does not succeed if fibrinogen prepared by precipitation with acid is added, either in the solid form or in alkaline solution, to a saline solution of fibrinoplastic substance. Fibrinogen ought therefore always to be prepared by precipitating with sodium chloride. The fibrin generators may, within certain limits, unite in very varying proportions to form fibrin. The author is unable to say whether the consistence, &c., of the fibrin depends on these proportions. Besides the fibrin generators, a third body is necessary to form fibrin, and this he regards as a ferment, because (1) a small quantity causes the formation of fibrin in a solution containing both generators as completely as a large one, but more slowly; (2) the activity of this substance increases with the temperature up to blood-heat, but above this limit its activity diminishes as the temperature rises, and it is completely destroyed at the boiling point. At zero its activity is much diminished, but is retained for an indefinite period; (3) after coagulation is finished, the fluid which remains when the fibrin has been removed will again cause coagulation in a fluid containing both generators. This ferment is not contained in coagulable fluids, so long as they are in the body, but is developed in them after they have been removed from it. Transudates contain both fibrin generators, as well as blood, but while the ferment begins to form immediately and increases very rapidly in blood, chyle, and lymph, it appears after several days only, and increases very slowly in transudates. They therefore serve admirably as reagents for the ferment, its presence being recognised by the increased rapidity of coagulation it produces. Commencing putrefaction somewhat hinders coagulation, but unless far advanced, will not prevent it after the addition of a large quantity of ferment. No difference can be detected between the ferments prepared from the blood of different kinds of animals. Either at or after the death of the tissues, some influence is exerted on the blood and transudates, which lessens the tendency of the ferment to develop in them. Blood or transudates which are removed from the body several hours after death, coagulate therefore slowly. The peri-

cardial fluid of the ox, or still better, of the horse, if not removed till ten or twelve hours after death, and kept at a temperature of 8°—10° C., can be kept for weeks without putrefying or showing a trace of coagulation till ferment has been added. The quickened coagulation which is caused in transudate by the addition of fibrinoplastic substance, and which the author formerly attributed to it, is really due to the ferment mixed with it. The addition of ferment alone to fibrinogen will not cause coagulation, as transudates containing only a small quantity of fibrinoplastic substance yield only a slight coagulum when ferment is added to them, and after its removal no further addition of ferment will induce coagulation again; but it will take place when more fibrinoplastic substance is supplied. These discoveries explain the apparently contradictory results of some of the author's former observations. The addition of concentrated solutions of neutral salts both prevents the development of the ferment and hinders its action when it is present. A fluid containing both fibrin generators without ferment can be prepared by letting blood flow directly from the vein of a horse into one-third of its bulk of a solution containing 1 part of magnesium sulphate in 3 parts of water. An aqueous solution of the ferment is obtained by treating 1 part of serum with 15—20 parts of strong alcohol for at least 14 days, filtering, drying the residue over sulphuric acid, pulverizing, treating for some time with distilled water, and filtering. The quantity of water used should be twice as great as that of the serum from which the ferment has been obtained. The ferment is contained in the filtrate, and is mixed with a small quantity of an albuminous body, which, however, is not fibrinoplastic substance. The ferment can also be extracted by glycerin after coagulation by alcohol, but not so readily as by water; and as the glycerin solution also contains an albuminous body, it possesses no advantages over an aqueous one. The author has not succeeded in preparing fibrinoplastic substance free from ferment. During the precipitation of fibrinoplastic substance it carries down ferment with it, but in greatly varying quantities. In order to destroy the activity of the ferment, the fluid containing it must be boiled for at least 5—10 minutes. At a temperature of 3°—5°, it retains its activity for an indefinite period if air be excluded, but loses it when exposed to air, and the more quickly the higher the temperature and the greater the surface in contact with air. The author details experiments which show that the ferment is not contained in an inactive state in the circulating blood, becoming active when it is drawn, but is formed only after the blood has been removed from the influence of the body. Its production continues until the whole of the fibrin has become coagulated, and then it ceases. The most active solutions of ferment are therefore obtained from serum immediately after coagulation has occurred. If allowed to stand longer, its activity is lessened by the exposure to air. Whipping the blood, and a temperature of 35°—40° C., increase the rapidity of the action of the ferment, but by thus hastening coagulation they lessen its production. A low temperature retards the action of the ferment, but it also lessens its production, and the best temperature for obtaining much ferment from horse-blood is 15°—22° C. The ferment is not contained in the red blood-corpuscles either before or after coagulation. The statement made by the author in a preliminary com-

munication that the ferment is developed by the action of the blood-corpuscles is erroneous. They quicken its action, but have no influence on its production. From experiments made with carbonic oxide and hydrogen, the author considers that coagulation cannot take place without oxygen, and that if the substances which take part in coagulation are deprived of oxygen for a long time, one or other, or all of them undergo such changes that they can no longer act after oxygen has been restored.

When a solution contains much fibrinogen and a small quantity only of fibrinoplastic substance, a quantity of fibrinogen remains after complete coagulation has taken place. If the quantity of fibrinoplastic substance is more than enough to produce coagulation of the fibrinogen, more fibrin will be formed than the fibrinogen will account for. The whole of the fibrinoplastic substance present never takes part in the formation of fibrin, a certain proportion always remaining in the solution. Apparently it is exposed to two opposite influences, one of which forces it to form fibrin, while the other strives to retain it in solution. What proportion goes to form fibrin is determined by the quantity of fibrinogen present. The proportion which remains in solution is determined by the solvent, and if we only knew what this is in natural solutions, coagulation might be entirely prevented by increasing its amount. When increasing quantities of fibrinoplastic substance are added to solutions of fibrinogen, the quantity of fibrin does not increase in proportion to the increase, but only in a constantly diminishing ratio.

Large quantities of water retard coagulation, and at the same time alter the relative proportions of fibrinogen and fibrinoplastic substance which take part in the formation of fibrin, that of fibrinogen being diminished, and that of fibrinoplastic substance increased. The fluid remaining after the fibrin has been removed from horse plasma, diluted with ten times its bulk of water, thus contains an excess of fibrinogen, and resembles many transudates.

The addition of fibrin-ferment to dilute plasma greatly accelerates coagulation, but does not increase the weight of the fibrin produced. When fibrinoplastic substance is added as well as ferment, the quantity of fibrin is distinctly increased. The increase of fibrin is much less than the weight of the fibrinoplastic substance added. The addition of fibrinoplastic substance in a solid form increases the quantity of fibrin more than the addition of a similar quantity in solution. Blood-corpuscles greatly accelerate coagulation. This is not due to their containing fibrin-ferment, but to an action of contact. They do not produce coagulation in coagulable fluids destitute of ferment. They contain no fibrino-plastic substance. Their action is due to hæmoglobin.

Hæmoglobin when purified, but not crystallised, accelerates the coagulation of plasma containing fibrin-generators and fibrin-ferment, but cannot act as a substitute for any of these or induce coagulation when either of them is wanting. So powerful is its accelerating action that the smallest quantity of fibrin-ferment acts with great rapidity in its presence. On this account plasma from horse-blood, collected directly from the veins in a saline solution, is not suitable for demonstrating the difference between the action of hæmaglobin and that of

fibrin-ferment. The presence of a very small quantity of ferment in a transudate, which also contains the fibrin-generators, can be detected by adding hæmoglobin to the liquid. The solution of hæmoglobin for this purpose may be prepared by pressing out the coagulum from horse's blood after it has begun to contract, and allowing the fluid to stand for a day or two at 8°—10° C. The blood-corpuscles then form a tough layer, which is to be freed from serum, washed, and stirred with 15—20 parts of water and then filtered to separate the remains of blood-corpuscles. By then precipitating with alcohol and extracting the coagulum with water a fluid is obtained which has not the slightest fermentative action.

Hæmoglobin and blood-corpuscles accelerate coagulation by *contact*, and do not undergo any change themselves. This power is also possessed by charcoal, platinum, asbestos, filter-paper, &c., and by other animal ferments. All substances which accelerate coagulation likewise decompose hydrogen peroxide. These two properties are inseparable from each other, and all bodies which decompose hydrogen peroxide accelerate coagulation. The rapidity with which they induce coagulation is also exactly proportional to the rapidity with which they decompose hydrogen peroxide. The most active substance is genuine uncrystallised hæmoglobin, then follow charcoal, platinum, washed fibrin, filter-paper, and asbestos. Animal ferments act with nearly the same rapidity as fibrin. Whatever destroys the action of any of these substances on hydrogen peroxide deprives them at the same time of their power to accelerate coagulation.

The author recognises two sorts of hæmoglobin: 1st, genuine hæmoglobin as it exists in the blood-corpuscles or as obtained from them by solution; and 2nd, crystallised hæmoglobin. Genuine hæmoglobin possesses in the highest degree the power of decomposing hydrogen peroxide and accelerating coagulation, but when crystallised it loses both of these properties. Genuine hæmoglobin is considered by the author to be amorphous, and he believes that it undergoes some change whereby it becomes crystalline before crystals actually form. This change is not produced only by those agents such as ether, which cause crystals to separate, but it takes place, though more slowly, under the influence of exposure to air, water, and a moderate temperature. Genuine hæmoglobin is not diffusible, and it is hardly oxidised at all by hydrogen peroxide. Conversion into the crystalline form, however, renders it diffusible through vegetable parchment (notwithstanding the contrary statement by Kühne and Preyer), and readily oxidizable by hydrogen peroxide, at the same time depriving it of its power to decompose hydrogen peroxide and accelerate coagulation.

Charcoal accelerates coagulation, but only a small quantity must be used, as it absorbs both fibrin-ferment and fibrin-generators. Charcoal which has been recently ignited and allowed to cool has no effect on coagulation, although it still decomposes hydrogen peroxide. This is not due to the formation of ash nor to expulsion of oxygen, but may possibly be attributed to increased power of absorbing the fibrin-ferment.

Platinum black accelerates coagulation, but must be used in still smaller quantities than charcoal. Fibrin always contains fibrin-ferment, from which it may be freed by soaking it for 24 hours in water acidulated

with acetic acid, and then washing it. When thus purified it has no action on fluids destitute of fibrin-ferment, but greatly accelerates coagulation in such as contain it.

Fibrin-ferment has no action on hydrogen peroxide. Ptyalin and pepsin decompose hydrogen peroxide, and they also accelerate coagulation.

Filter-paper decomposes hydrogen peroxide and quickens coagulation. The latter action is due partly to the paper itself and partly to a diastatic ferment contained in it. This ferment can be removed by water or watery fluids, and when these are passed through a filter, they acquire the power of converting starch into sugar and of accelerating coagulation. Plasma coagulates much more quickly on account of the ferment it takes up when it is filtered through paper.

The ferment is destroyed by boiling. In all experiments on coagulation, where it is necessary to filter the liquids employed, the filters must be previously boiled in water in order to avoid the error which would otherwise arise from the presence of the ferment.

Vegetable parchment has a similar action to that of filter-paper. This is due partly to the paper itself and partly to some substance which adheres to it. The discovery of this fact renders the author's former statement that fibrinoplastic substance diffuses through vegetable parchment very doubtful, as it was chiefly founded on the observation that coagulation occurred rapidly in the fluid he employed when a dialyser containing fibrinoplastic substance was placed in it. He now finds that the same effect is produced by an empty dialyser or one containing water.

The accelerating action of hæmoglobin, charcoal, &c., on coagulation is not due to the oxygen they contain, as the author in his preliminary notice (see vol. xxv, p. 643, of this *Journal*) supposes it to be. This is shown by the fact that charcoal, which has again absorbed oxygen after ignition, does not accelerate coagulation, while its power to do so is not impaired after complete removal of its oxygen by boiling it with water for 2—3 hours. Carbonic-oxide-hæmoglobin accelerates coagulation as much as oxy-hæmoglobin. It seems, however, that a minute quantity of oxygen is necessary to coagulation. The plasma generally contains enough, and when this is the case coagulation occurs whether the hæmoglobin contains oxygen or not. When the plasma does not contain enough, coagulation does not occur unless oxygen is supplied. Inasmuch as the blood-corpuscles and hæmoglobin may supply a minute quantity of oxygen necessary to the plasma, they may, under certain circumstances, be essential to coagulation, but this function can be performed by the atmosphere, although exposure to air has nothing to do with the acceleration which hæmoglobin produces after coagulation has once been induced.

T. L. B.

On the Nutrition of Muscular and Pulmonary Tissues in Health and when affected with Disease from Phthisis. Part II. By Wm. Marcet (Phil. Mag. [4], xliv, 443—457).

The parenchyma of the lungs contains a much larger proportion of nutritive, and much less waste material than muscle. This seems to show that the nutrition of pulmonary tissue is more rapid than that of

muscle. While in muscles the phosphoric acid and potash are eliminated as a crystalloïd phosphate, in the lungs the potash is probably eliminated as a crystalloïd carbonate due to the action of the carbonic acid emitted from the blood during its circulation through the lungs.

Wheaten flour, potato, and rice contain different proportions of phosphoric acid and potash, but the ratio of total to colloid phosphoric acid and potash in these three kinds of vegetable food remain very nearly the same.

In phthisis, muscular tissue contains less nutritive and less mature or insoluble material than in health, rather more water and a much higher proportion of chlorine and soda. It contains phosphoric acid and potash effete in the exact proportion to form a pyrophosphate, just as in health. This shows that the process of waste in muscles takes place in phthisis precisely as it does in health. The emaciation in phthisis appears due mainly to the blood not being in the proper condition to supply nutritive material to muscular tissue. The damp or wet state peculiar to muscles after death from phthisis, appears to show that the colloïd state of flesh in that disease is somewhat deficient.

The tubercular or adenoïd formation in pulmonary tissue actually undergoes nutrition, and is consequently a growth, the phosphoric acid and potash being apparently eliminated as in the case of flesh in the form of a crystalloïd phosphate. The nutrition of the abnormal growth accounts for the absence of any smell of decomposition when the body is examined shortly after death. The softening of tubercular substance appears due to a loss of colloïd power, and can hardly be due to an increased proportion of water, as this is very small. There is, apparently, no increase of fat in tubercular pulmonary tissue, but as diseased lungs contain rather more water than healthy lungs, tubercular matter contains proportionally to its dry residue a little more fat than healthy pulmonary tissue under the same circumstances.

In nature, soluble matter continually undergoes transformation from crystalloïd to colloïd, and from colloïd to crystalloïd. Animal secretions and the products of decomposition of animal and vegetable tissues are crystalloïd, admitting of ready distribution through land and water by a physical process of diffusion. These crystalloïd substances are transformed into colloïds by plants and used in that form as food for animals, and both plants and animals yield them back again in their original crystalloïd state. Sodium chloride appears to be the only exception to this rule.

T. L. B.

Contributions to the Physiological Chemistry of Milk. By F. SOXHLET (Journ. f. pract. Chemie. [2], vi, 1—52).

SOXHLET investigates the question as to the identity of casein and alkali-albuminate, concerning which there exist considerable differences of opinion.

He first discusses the relation of alkaline phosphates to alkali-albuminate.

Hoppe-Seyler opposes the identity of casein and alkali-albuminate

on the ground that in the milk no alkali-albuminate can be present, inasmuch as the fluid generally has an acid reaction, whereas solutions of the latter substance are precipitated even on neutralisation. Rollett, however, has proved that solutions of alkali-albuminate are not precipitated by acids in presence of neutral sodium phosphate, and it is owing to the presence of such phosphates in the milk that casein, which behaves exactly like alkali-albuminate, is not precipitated, even though the milk exhibits an acid reaction. Following out Rollett's researches Soxhlet seeks to determine the quantitative relation of the acids and salts in the liquids in which, notwithstanding an acid reaction, no precipitation of albuminate occurs. By experiments with volumetric solutions of neutral sodium phosphate, acid potassium phosphate, neutral sodium sulphate, sulphuric, acetic and phosphoric acids, he arrives at the result, that on the addition of an acid to a solution of alkali-albuminate in presence of neutral sodium phosphate, the albuminate begins to be precipitated at the moment when all the neutral phosphate has been converted into the acid salt. The quantity of acid required for precipitation stands in intimate relation to the quantity of alkaline phosphate present, and the precipitation depends, not on the absolute amount of acid phosphate formed, but on its relative proportion to the neutral phosphate still remaining. The sodium sulphate which is formed when sulphuric acid is added to the albuminate solutions in neutral sodium phosphate, is without influence on the precipitation of the albuminate.

A relatively small amount of acid phosphate causes precipitation in pure alkali-albuminate solutions. In order to cause precipitation when neutral phosphate is present, a much larger proportion of the acid salt is required, because if the former is in excess, the albuminate remains in solution. In order to cause precipitation, it was found that acid phosphate of alkali-metal must be added until the quantity of neutral phosphate, which is formed from the base of the alkali-albuminate and from a part of the acid phosphate, stands in the relation of one molecule to thirty-two molecules of the acid phosphate. If more neutral phosphate is present than is expressed by this proportion, no precipitation occurs.

Reaction of the Milk and other Animal Fluids.—The solution of casein in milk with an acid reaction must, as shown by the foregoing experiments, depend on the simultaneous presence of a certain proportion of neutral phosphate together with the acid phosphate which gives the acid reaction. Such solutions, however, exhibit not merely an acid but also an alkaline reaction at the same time. And this is really the case with the milk, for it at the same time reddens blue litmus and turns red litmus-paper blue. This *amphoteric* reaction of milk can be demonstrated best on gypsum plates coated with litmus, after the manner suggested by Liebreich. To this amphoteric reaction of the milk, the author ascribes the different statements made in regard to the normal reaction of the fluid. The alkaline reaction becomes more evident when the milk is heated. The same is shown by very dilute solutions of so-called neutral sodium phosphate and caustic soda. Violet solutions of litmus also become more blue on heating. The change is not due to concentration by evaporation, as the original

colour reaction returns on cooling. Fluids which contain vegetable albumin become more alkaline when heated, and it has been supposed that this is due to the liberation of an alkali when the albumin is coagulated. That it is not due to this cause is proved by the fact that solutions free from albumin, but containing the same salts as the albuminous liquids, likewise exhibit the same intensification of the alkaline reaction when heated. A similar explanation is given of the fact observed by Du Bois Reymond, that a muscle dipped in boiling water becomes more alkaline than before.

In connection with the amphoteric·reaction of animal fluids, difficulties are pointed out in the estimation of the so-called free acid of the urine. The presence of acid sodium phosphate in the urine renders it difficult to say exactly when all the acid is neutralised by the addition of alkali, because it is impossible to hit a point when the liquid will react exactly neutral, as there is no solution of a phosphate which reacts precisely neutral.

A third objection to the identity of casein and alkali-albuminate is supposed to exist in the different behaviour of these two substances towards rennet. Milk is coagulated, while alkali-albuminate is not. It has been shown, however, that alkali-albuminate is coagulated by rennet when milk-sugar has been added to the solution. Soxhlet agrees with Simon in referring the coagulation to the lactic acid developed by the action of rennet on milk-sugar. Heintz, however, and subsequently Völcker found that casein might be coagulated by rennet, and yet the fluid remain alkaline, and hence considered that rennet may coagulate casein, not only by the formation of lactic acid, but also by some specific action. For this specific action a higher temperature is necessary. Soxhlet explains the differences by the amphoteric reaction. Rennet developes lactic acid from the milk-sugar, by which the neutral alkaline phosphate of the milk is converted into acid phosphate. When in consequence of this acidification, that relation between the neutral and acid phosphate is established in which the albuminate remains just dissolved and no more, then when the temperature is raised albumin is precipitated while the fluid is still alkaline. Along with the alkaline reaction, however, an acid reaction is also to be observed. This, however, had not been noticed by former observers.

The statement that the casein precipitated by acid is easily soluble in sodium carbonate, while that precipitated by rennet is not so, depends merely on the physical, and not on any chemical differences of the precipitate.

Rennet belongs most probably to the non-organised ferments. Zahn states that alkali-albuminate may be filtered through porous earthenware, but casein not; and considers this to be a proof against the identity of the two substances. Soxhlet shows that this depends on the presence of fat-globules in the milk, and finds that alkali-albuminate, when emulsionised by fat, is likewise incapable of filtration (or with difficulty) through such earthenware cells.

Zahn also states that the casein of the milk can be precipitated by sodium carbonate, but that solutions of alkali-albuminate cannot. This, however, does not depend on any chemical difference between the two substances, but on the fact that in the milk other substances are

present. The precipitation of casein from milk may likewise be effected by caustic alkalis and sodium phosphate, as well as by sodium carbonate. The cause of the precipitation is the formation of calcium phosphate, which carries down the albuminate mechanically in the form of a finely granular precipitate. If alkali-albuminate is treated with calcium chloride and emulsified with fat, a like precipitate is caused on the addition of sodium phosphate. The statement made by Hoppe-Seyler that alkali-albuminate does not, like casein, yield potassium sulphide when treated with caustic potash, Soxhlet finds to be incorrect. He obtained a distinct evolution of hydrogen sulphide on the addition of acetic acid to the mass resulting from the treatment of alkali-albuminate with concentrated caustic potash.

Still, another difference is stated by Hoppe-Seyler to exist between casein and alkali-albuminate, namely, the specific rotation exerted by these two substances on a ray of polarised light. Soxhlet thinks that this is no sufficient ground for establishing a chemical difference between the two, because the specific rotation is liable to be greatly influenced by the presence of salts and by other conditions of the solutions.

From these various considerations the author comes to the conclusion that casein and alkali-albuminate are identical in every respect.

D. F.

Analytical Chemistry.

Detection of Bromine in presence of Urea. By G. Bizio (Gazzetta Chimica Italiana, ii, 339—343).

The colour imparted by bromine, as well as by iodine, to chloroform or carbon sulphide, is destroyed by agitation with urine, and this decolorising action has been attributed partly to uric acid and its salts, partly to the colouring matters of the iodine or bromine, being supposed to fix itself on these constituents of the urine. There is, however, a difference in the behaviour of the two haloïd elements under these circumstances, iodine when thus fixed being liberated with comparative facility by chlorine or by bromine, whereas the liberation of bromine by means of chlorine is more difficult. When equal quantities of potassium bromide are dissolved in equal volumes of distilled water and of urine, and the two solutions, after addition of carbon sulphide, are treated with chlorine-water, the former acquires a splendid red colour on addition of a single drop of the reagent, whereas the latter (the one containing the urine) requires a considerable quantity of chlorine-water before it exhibits any colour at all, and even then the tint is not red, but only sulphur-yellow.

This difference is attributed by the author to the action of urea. He finds that this substance does not interfere with the liberation of iodine from its compounds by chlorine-water. Two test-tubes containing equal quantities of potassium iodide dissolved in equal volumes of water, the one pure, the other containing urea, exhibited exactly the same depth of violet colour when chloroform and a few drops of chlo-

rine-water were added to each of them. But when a similar experiment was made with bromide of potassium, the result was very different, the chloroform in the tube containing the pure aqueous solution of the bromide acquiring a splendid orange-red colour on addition of chlorine-water, whereas that in the tube containing the solution to which urea had been added acquired only a yellow colour. It is probable that urine contains also other substances capable of exerting this peculiar action on bromine, which appears to be different from that which is exerted by uric acid and the urinary pigments.

The author thinks that this action of urea on bromine, and the uncertainty of the colour-reactions thence resulting, may afford some explanation of the different results obtained by Pelloggio and Giannetti (p. 1125 of last volume) in testing urine for iodine with bromine-water.

Lastly, with regard to the detection of very small quantities of iodine in urine by this reagent, he observes that if the urine be previously dialysed so as to separate the urea, the great care which Giannetti thinks it necessary to observe in agitating the liquid is no longer required; indeed, the liquid may then be briskly agitated, with the certainty of obtaining a decided result, especially if chloroform has been added to dissolve the liberated iodine instead of carbon sulphide. On the whole, however, he considers chlorine-water a better reagent than bromine-water for the detection of iodine in urine.

H. W.

Testing of Potassium Bromide. By Falieres (Chem. Centr., 1872, 425).

The method is the same as that of Bouis for the iodide. Chloride is indicated, in the absence of other salts, when more than the calculated quantity of a standard solution of silver nitrate is required for precipitation; hydrates or carbonates of the alkalis by placing a small fragment of iodine in the solution: if they are absent, coloration will be observed. Colourless hydrochloric acid changes to yellowish-green in presence of bromate. When nitrate is present, bromine and nitrogen tetroxide escape on addition of sulphuric acid.

A. T.

Testing Potassium Iodide for Iodate. By E. Schering (Dingl. Polyt. J., ccv, 490).

Potassium iodide containing iodate is coloured yellow by hydrochloric acid; if, however, the acid be not free from chlorine, pure iodide will show the same reaction when mixed with it. To avoid the possibility of this error, a crystal of tartaric acid is placed in the solution of this salt, when the presence of iodate is discovered by the formation of a yellow zone round the crystal.

W. S.

Pyrometric Examination of Dinas Bricks and their Raw Material. By CARL BISCHOF (Dingl. Polyt. J., ccv, 120—124).

PORTIONS in the form of fragments, and others in fine powder, were exposed to temperatures described as "near the melting point of platinum," or "full fusing heat of platinum," and the change of appearance of the specimens noted. The observations are not worth reproducing.

C. H. G.

Estimation of Zinc by means of a Stream of Hydrogen. By M. BURSTYN (Dingl. Polyt. J., ccv, 440).

THE author, referring to Bobierre's method for thus separating zinc from copper, lead, and iron, says that if not more than 2—3 per cent. lead be present, this is invariably carried away along with the zinc; if lead be present in greater quantity, part of it remains behind.

M. M. P. M.

Loss through Volatilisation in the Cornish Copper Assay. By C. A. MAHONY (Chem. News, xxvi, 243).

THE author objects to the dry Cornish assay as a means of estimating the value of copper ores, inasmuch as a certain percentage of copper is invariably lost by volatilisation in the form of chloride.

This loss of copper takes place in the fusion for "coarse metal" and "refining of regulus." It is due to the circumstance that the copper oxides are reduced, and the crude button of metal subsequently refined in presence of a large proportion of sodium chloride, when, owing to the high temperature at which the reduction is effected, a small quantity of copper chloride is formed and volatilised.

In order to prove the volatilisation of copper when fused with sodium chloride, the following experiments were undertaken:—

A button of pure copper, weighing 49·51 grs., was fused with 240 grs. of salt. The loss was 0·33, 0·34, 0·21, and 0·42 grs. respectively, for five minutes' fusion.

Another button, weighing 48·32 grs., lost 0·31, 0·33, 0·32 grs. with 480 grs. sodium chloride.

The following table shows the loss actually sustained in the dry assay of three samples of copper pyrites:—

Percentage from Button.	Percentage in Slag.	Total percentage.	Percentage by Wet Assay.	Loss.
10·12	0·07	10·19	11·25	1·06
8·88	0·12	9·00	10·20	1·20
13·88	0·27	14·15	15·00	0·85

The author has up to the present time been unable to devise a substitute for sodium chloride.

J. W.

Estimation of Manganese in Soils and Vegetables.
By A. Leclerc (Compt. rend., lxxv, 1209).

The process recommended is, in the case of a soil, to destroy the organic matter by ignition and digest in a slight excess of nitric acid. The chlorine is to be removed by silver nitrate, and the manganese converted into potassium permanganate by means of minium. The solution, which should contain free nitric acid, is then titrated by a standard solution of mercurous nitrate, the value of which has been previously estimated by a known solution of permanganate. This method is said to be much superior to others, especially in cases where the amount of manganese present is very small.

J. B.

Action of an Alkaline Copper Solution on Cane Sugar and on Mixtures of Cane and Grape Sugar. By C. Scheibler (Deut. Chem. Ges. Ber., v, 928).

The author refers to a communication by E. Feltz to the Paris Academy on the 21st October, in which it is stated that cane sugar also reduces an alkaline solution of copper, and that consequently the determination of grape sugar in presence of cane sugar by Trommer's reaction gives results which are too high. The author remarks that in 1869 in the *Zeitschr. des Vereins f. d. Rubenzucker-industrie, im Zollverein* (Bd. xix, 386), he drew attention to the same fact, and showed how the amount of cuprous oxide separated was entirely dependent on the duration of the operation.

H. E. A.

Distinction between Creasote and Phenol.
(Ding. Polyt. J., ccv, 494).

Beechwood-tar creasote is almost insoluble in glycerin; phenol, on the contrary, dissolves therein in all proportions. If a large proportion of phenol is mixed with the creasote, the latter also dissolves in the glycerin with the phenol.

W. S.

Detection of Prussic Acid in Cases of Poisoning. By Almen (Dingl. Polyt. J., ccv, 496).

Paper saturated with cupric sulphate and tincture of guaiacum, is recommended as a preliminary test. Such paper is turned blue by prussic acid, and is said to afford so delicate a test of its presence, that if it gives a negative result, further investigation may be regarded as superfluous. If, on the other hand, it indicates the presence of prussic acid by the production of a blue colour, confirmation of the result must be sought by distillation and the application of the well-known tests, the sulphocyanate reaction being the most delicate.

W. S.

Separation and Detection of Strychnine in Chemico-legal Investigations. By H. St. Clair Glay; also by Lyman (Chem. Centr., 1872, 426).

H. St. Clair Glay rubs the mass to a paste with water, digests for 24—27 hours with an excess of acetic acid, and dialyses.

Lyman digests for 14 hours with water containing acetic acid, treats it with potassium, and agitates with chloroform.

A. T.

The Testing of Bees-wax for Adulterations. By E. Donath (Dingl. Polyt. J., ccv, 131—137).

The substances used as adulterants are paraffin, tallow, stearic acid, Japanese wax, and resin, of which paraffin is the one that can be present in the largest quantities without causing an alteration of appearance. The following series of tests is found by the author to serve the purpose of detecting any one of them:—

A nut-sized piece of the wax in question is boiled for five minutes with a concentrated solution of sodium carbonate.

A. An emulsion which remains on cooling is formed: the wax is adulterated with *resin*, *tallow*, *stearic acid*, or *Japanese wax*.

B. The wax floats as a distinct layer on a slightly yellow liquid: it is pure or adulterated with *paraffin* only.

In the case of A, the wax is boiled with a moderately concentrated solution of caustic potash, and salt is afterwards added. If a coarsely flocculent precipitate of soaps is formed, all the substances named in A may be present, with the exception of Japanese wax, which gives rise to a small grained magma, which is very characteristic to any one who has previously made a trial experiment. A determination of the specific gravity of the wax is next made: if it be found greater than 0·970, Japanese wax is almost certainly present; if less than 0·960, paraffin is the adulterant, supposing that the other bodies named in A are absent. If the preliminary tests have shown the presence of tallow, resin, &c., each must be tested for separately, thus—

Resin.—Boil the wax with concentrated nitric acid; cool the mixture; pour off the acid; and dilute with water. If resin were present, a yellow flocculent precipitate soluble in ammonia to a blood-red liquid, is formed.

Stearic Acid.—The wax is boiled for three-quarters of an hour with twenty times its weight of alcohol; the whole allowed to cool for several hours, and the alcohol poured off and mixed with water. Any stearic acid is precipitated in flocks. One portion of the alcoholic solution is tested with an alcoholic solution of acetate of lead, which gives a thick precipitate if stearic acid be present.

Tallow is tested for in the same way as stearic acid. Water causes a milkiness in the alcoholic solution, but the acetate of lead gives nothing more than a slight yellow precipitate.

C. H. G.

Analysis of Soaps. By F. Jean (Chemical News, xxvi, 206).

The author refers to the adulteration of soaps with resin, and to the difficulty of detecting and estimating this adulterant; he has carefully examined the properties of resins, and finds that on boiling with caustic soda-lye under a pressure of three atmospheres, resin is saponified, yielding (1), a resinate insoluble in alkalies; (2), a soluble resinate; (3), a substance which is not separated from its acid solution. Upon these results the following process for the estimation of resinous matters in soaps is based:—

10 grams are dissolved in 100 c.c. distilled water, and a slight excess of strong caustic soda solution is added; the soap of the fatty acids is thereby precipitated, together with the resinate (1), and separated by filtration, and washing with caustic soda-solution. The alkaline filtrate is acidulated with dilute sulphuric acid, and the resinate (2) which then precipitates is collected on a previously dried and weighed filter. The acid filtrate must now be saturated with soda (any precipitate which may form, collected on the weighed filter along with (2)), evaporated to dryness, treated with alcohol, and the solution again evaporated in a previously weighed porcelain dish; this residue = resinoid matter + glycerin. At a boiling heat glycerin decomposes iodic acid, iodine being set free; it may thus be recognised.

The first precipitate, resinate (1) and fatty acids, is dissolved in boiling water and precipitated by a slight excess of barium chloride; from this precipitate, after washing and drying at 100°, the resinate of barium is dissolved out by means of ether; this solution is evaporated to dryness, the residue dissolved in boiling water, and the resin, being set free by means of a few drops of sulphuric, is collected on the filter already containing resinate (2), washed, dried, and weighed. By boiling the acidulated solution, the baryta soap is decomposed and the fatty acids set free, which may then be collected and weighed.

To estimate the alkali, the author dissolves 2—3 grams of the soap in alcohol, and passes carbon dioxide through this solution on the water-bath, whereby the alkali is thus carbonated. By filtering, boiling the filtrate to drive off alcohol, adding 5—10 c. c. titrated sulphuric acid, boiling, cooling, filtering from fatty acids, and estimating excess of sulphuric acid by soda solution, the amount of alkali combined with the fatty acids is found.

The uncombined alkali is estimated in the matter insoluble in alcohol obtained by passing carbon dioxide through a solution of the soap.

12·6 parts alkali (soda) combine with 100 parts anhydrous fatty acids. The quantity of combined alkali, therefore, is multiplied by 100, the product divided by 12·6, and thus the anhydrous fatty acids are found. This, with alkali subtracted from 100, gives water and impurities.

To estimate water, 1—2 grams is dissolved in the smallest possible quantity of strong alcohol in a weighed dish, a weighed amount of fine dry sand added, and the whole dried at 110°.

M. M. P. M.

Note on Litmus-paper. By Ed. R. Squibb (Chemical News, xxvi, 247).

To prepare good litmus-paper, the following formula may be adopted:—

Good litmus, in fine powder	1 part,
Water	4 parts,
Alcohol..............................	1 part,

all by weight. Put the ingredients into a bottle, and shake occasionally during 24 hours; allow the sediment to settle completely, and decant the clear liquid. Put the same quantity of water and alcohol upon the sediment, and treat as before, using this second liquid to dilute the first portions if necessary. Separate about one-fourth part of the first clear liquid, and add to the remainder dilute sulphuric acid, until it assumes a purplish-blue colour; then add one-half of the previously separated portion; should this addition completely restore the pure blue colour, again neutralise it with dilute sulphuric acid, and finally add the remaining eighth part of the original solution. Dilute this liquid with water, or with the second liquid from the litmus sediment, until a slip of paper dipped into it acquires a pale purplish-blue colour.

The solution for red litmus-paper will not bear the same amount of dilution as that for the blue, and must be made of the proper purplish-red colour by the addition of dilute acid before dilution. Litmus solutions so made will keep almost indefinitely.

J. W.

Technical Chemistry.

Causes of the Loss of Sodium in the Manufacture of Soda by Leblanc's Process. By A. Scheurer-Kestner (Compt. rend., lxxv, 1184—1186).

By recent experiments the author has proved:—

1stly. That no loss of soda salt occurs as sodium reduced and volatilised in the black-ash process.

2ndly. That the greater part of the loss is due to the formation of insoluble sodium compounds, which remain behind in the soda-waste after lixiviation of the black ash or crude sodium carbonate.

It has been further found that the quality of coal used as reducing agent, does not affect the amount of soda retained by the soda-waste, but that this loss increases *proportionately* with the excess of limestone or chalk employed; this is shown in the following analyses, made on soda-waste dried at 100°:—

Limestone used for 100 sodium sulphate.	Sodium retained by the waste (100 parts).
98·0	0·59
102·0	0·86
107·5	1·27
111·0	1·30

The greater part of the excess of limestone is converted into lime during the black-ash fusion. The lime thus formed during lixiviation of the black ash, becomes hydrated, and reacts at the same time upon the sodium carbonate, rendering a portion of that salt insoluble in water. Well-made black ash is quite porous, the dense material retaining the alkali more persistently. The waste from porous black ash was found to contain 1·44 p. c., and from a dense sample, 1·97 p. c. of sodium. The remedy to be employed to avert this loss as far as possible, is simply to use the least possible excess of limestone or chalk requisite for the complete reaction in the black-ash furnace.

W. S.

Constitution of the Liquors obtained by the Oxidation and Lixiviation of Soda-waste in the recovery of Sulphur therefrom. By C. STAHLSCHMIDT (Dingl. Polyt. J., ccv, 229—247).

THE author sets out with a description of the two processes generally known and adopted for sulphur recovery, viz., that of Guckelberger and Mond, and that of Schaffner. Both methods are not unfrequently combined into one process. The waste is placed in vats, and air is blown through the mass for 12 to 16 hours; weak liquors from former lixiviations are then poured on and allowed to drain through, and these washings are repeated till a strength of 10° to 12° Baumé is obtained in the liquor drawn off. The sulphur liquors and hydrochloric acid of 20° Baumé are now mixed together in the precipitation vat, additions of each being made alternately in the proportion of about 8 : 1 or 7 : 1. During the mixing the agitator is set in motion, and the liquor kept well stirred up till the vat is filled. The mixture is then heated to 60° C., well agitated, and more acid added till a sample of the liquid smells unmistakeably of sulphurous acid. The sulphur sinks quickly and almost completely to the bottom of the vats. It is collected, drained, and thrown into the Schaffner's refining apparatus.

According to Mond, calcium sulphydrate and bisulphide are formed in the course of oxidation of the waste, and subsequently are oxidised to calcium thiosulphate. A portion of this decomposes again to calcium sulphhydrate and calcium sulphite; the last-named body, being insoluble, occasions loss of sulphur. The liquors obtained always contain calcium thiosulphate, sulph-hydrate, and polysulphide of the formula CaS_2 (Mond).

Mond's theory, which is supported by experiment, is as follows:—The decomposition of the liquors by hydrochloric acid does not result in the splitting up of calcium thiosulphate into calcium sulphite and sulphur ($CaS_2O_3 = CaSO_3 + S$), but into calcium trithionate, with which a small quantity of calcium pentathionate is mixed ($5CaS_2O_3 + 6HCl = 3CaCl_2 + 3H_2O + 2CaS_3O_6 + 4S$). The trithionate is then decomposed by heating into calcium sulphate, sulphur, and sulphurous acid. This sulphurous acid then reacts upon another portion of thiosulphate, forming trithionate, with separation of sulphur ($2CaS_2O_3 + 3SO_2 = 2CaS_3O_6 + S$). The trithionate is then decomposed, as above mentioned, and the presence of calcium sulphate amongst the precipi-

tated sulphur is thus explained. Schaffner opposes this view, and states that the formation of calcium sulphate is due to the presence of sulphuric acid in the crude hydrochloric acid used in the decomposing process. The author experimentally proves Mond's theory to be the correct one.

Schaffner considers that by the oxidation of the waste, calcium thiosulphate and the polysulphides, CaS_2 and CaS_3 are formed.

The difference in the composition of the liquors depends upon the time taken in the oxidation, the temperature, and partly on the degree of humidity of the waste.

Vauquelin found in 1817 that no calcium polysulphides could be obtained by the dry method. Buchner, 1816, and Herschel, 1820, obtained in the wet way crystallised compounds of calcium and sulphur. H. Rose in 1842 also obtained, by another method, crystals having the formula $CaS_5.5CaO + 20H_2O$.

Schöne found that solutions of calcium polysulphides never yield pure polysulphides on evaporation. On the contrary, they are decomposed by water, with evolution of hydrogen sulphide, and with separation of a solid mass, which consists of calcium hydrate and sulphur. Pure calcium monosulphide was prepared and boiled with different proportions of water and sulphur. It was then found that the calcium cannot exist in solution with less than four molecules of sulphur, and that if less than three molecules of sulphur to one molecule of calcium sulphide were brought into contact with water, only so much calcium sulphide dissolved as was necessary to form the tetrasulphide, the remainder being indifferent to the sulphur, and decomposing in contact with the water into calcium hydrate and sulph-hydrate, which first partially, but at last entirely dissolves with the tetrasulphide—

$$(1)\quad 6S + 6CaS + 4H_2O = 2CaS_4 + 2CaH_2S_2 + 2CaH_2O_2.$$
$$(2)\quad 12S + 6CaS + 2H_2O = 4CaS_4 + CaH_2S_2 + CaH_2O_2.$$
$$(3)\quad 18S + 6CaS = 6CaS_4.$$

In reactions 1 and 2 the calcium sulph-hydrate is recognised on addition of manganese sulphate. In the solution 3, however, only traces of this compound were detected. The tetrasulphide can dissolve a molecule of sulphur, and more with heat, and it thus entirely corresponds with the sulphur compounds of strontium and barium. Like these compounds the calcium tetrasulphide has, though in far higher degree, the power of forming crystalline compounds with lime, as observed by Herschel and Buchner, and later by H. Rose. Schöne obtained the compound $3CaO.CaS_4 + 12H_2O$ by boiling pure burnt lime with sulphur and much water for an hour; the hot filtered solution was then allowed to stand after addition of calcium hydrate. The presence of lime and calcium thiosulphate is necessary for the formation of this compound.

By passing hydrogen sulphide through lime-milk for several days, and setting aside the filtered solution for six months in an almost airtight vessel, then evaporating to half the volume, and leaving the liquid to stand some weeks, Schöne obtained orange-yellow prismatic crystals of the formula $4CaO.CaS_4 + 18H_2O$. The formation of both these salts is

generally dependent upon the presence of a sulph-hydrate, or a thiosulphate.

The amount of sodium compounds present in soda-waste is generally so great as to be equivalent to 4 to 5 per cent. of sodium sulphate, and in the oxidation process these sodium salts are almost entirely dissolved. By allowing the oxidised liquors to stand in a closed vessel for several months, air being excluded, splendid orange-coloured acicular crystals were obtained, having the composition $4CaO.CaS_4 + 18H_2O$.

These crystals in a damp place gradually decompose and turn white. On warming them with water, entire decomposition takes place, with formation of calcium hydrate and sulphur, and liberation of hydrogen sulphide. The salt is much more stable in a dry atmosphere. Placed over sulphuric acid it gives off hydrogen sulphide and the crystals assume a darker tint. If the clear sulphur-liquors be treated with absolute alcohol, almost immediately crystalline plates and needles of a yellow colour are formed, developing, on standing, into thin plates. On analysis these were found to contain 17·10 per cent. S., 27·6 Ca., and 44·2 H_2O, and behaved with reagents like the last-named compound, the oxytetrasulphide. The oxytetrasulphide treated with hydrochloric acid deposits sulphur, and in the decomposed liquor hydrogen trisulphide has been recognised by A. W. Hofmann, and on this account the amount of precipitated sulphur is smaller than that which accords with the calculation. Direct estimation gave 12 per cent. of sulphur, whilst the formula for the three molecules requires 13·4 per cent. If the liquor be concentrated over sulphuric acid, it is decolorised, with separation of sulphur, and in the solution thiosulphates and sulphates are present.

The liquors treated with alcohol, and freed to a certain extent in this way from the oxytetrasulphide, were further treated with absolute alcohol as long as a precipitate fell; thus a yellow precipitate was obtained, afterwards becoming white. It is insoluble in water, but dissolves completely in hydrochloric acid, sulphurous acid being given off, and was proved to be calcium sulphite, $CaSO_3 + \frac{1}{2}aq$.

The once precipitated calcium sulphite is not redissolved on addition of large quantities of fresh liquor; and it is considered likely that the calcium sulphite is not free, but in chemical combination with some other sulphur compound, the compound being decomposed by the alteration in the solvent. Thus Kuhlman has observed a compound of this kind in beautiful yellow crystals, of the formula $CaSO_3 + 2CaS + 6aq$, on old heaps of soda-waste. The liquor which had been precipitated with alcohol, was allowed to stand for several months in a closed flask, when sodium thiosulphate crystallised out. By passing carbon dioxide in excess through the sulphur liquors, and then boiling, a yellow precipitate of pure calcium carbonate and sulphur is obtained, together with a clear filtrate containing a little sodium carbonate and large quantities of sodium thiosulphate. The sodium sulphur-compounds are thus converted into sodium carbonate, which coming in contact with calcium thiosulphate formed from calcium sulphite is decomposed with precipitation of calcium carbonate, the excess of sodium carbonate remaining in the liquor. If the above experiment be performed after freeing the liquor from calcium salts by treatment with excess of alcohol, a pre-

cipitate is obtained of pure calcium carbonate and sulphur. The filtrate is coloured yellow by dissolved sulphur, and becomes olive green on heating. On addition of water precipitation of sulphur takes place, and on evaporating, sodium carbonate and thiosulphate crystallise out. If the liquor is shaken with carbon sulphide and the latter evaporated, a residue of pure sulphur is obtained, proving that free sulphur had been dissolved by the polysulphides of calcium present. On treating it with manganese solution, hydrogen sulphide was liberated, proving the presence of sulph-hydrates.

25 c.c. of the sulphur liquor were found to contain as follows:—CaS_n, 0·309 grm.; $4CaO.CaS_4$ + 18 aq., 1·106; $CaSO_4$, 0·0333; $CaSO_3$, 0·275; $Na_2S_2O_3$, 0·8453; CaH_2S_2, 0·0704; NaHS, 0·3869.

W. S.

Composition of Chloride of Lime. By J. Kolb (Compt. rend., lxxv, 1181—1184).

In this paper a process devised by Calvert for the analysis of chloride of lime is criticised. Calvert concluded, from experiments made by this method, that chloride of lime has the composition $CaO\ Cl_2O + 2CaCl_2$. The author, however, by observing the amount of chlorine absorbed by calcium hydrate concludes that the formula is $CaO.Cl_2O + CaCl_2$, and this conclusion he confirms by several other observations. The analyses of good samples of bleaching powder from numerous localities show indeed that the quantity of chlorine in the hypochlorite of calcium scarcely ever exceeds that belonging to the chloride by more than 1 or 2 per cent., so that the composition may be approximately represented by $100CaOCl_2O + 102CaCl_2$, and certainly not $100CaOCl_2O + 200CaCl_2$, as would accord with Calvert's views. Calvert's theory is controverted by the following fact, that when 1 litre of chlorine is absorbed by lime, on treating the chloride of lime obtained with hydrochloric acid, the whole litre absorbed is liberated again, and not merely $\frac{2}{3}$ litre, as according to Calvert. This fact can only be explained by the equation, $CaOCl_2O + CaCl_2 + 4HCl = 2CaCl_2 + 2H_2O + 4Cl$.

The author next examines the analytical method devised and employed by Calvert, and there discovers the cause of the erroneous theory set forth. This method is as follows:—The filtered chloride of lime solution has a current of carbonic acid blown through it, which does not affect the calcium chloride, but decomposes, the hypochlorite forming calcium carbonate, the weight of which indicates the quantity of lime combined to form hypochlorite, and thus the amount of hypochlorite. The filtered liquid contains the calcium chloride, which is estimated in the usual way. The method adopted by the author is as follows:—The powdered chloride of lime is dissolved and filtered. A portion of the filtrate is treated with ammonia, and afterwards heated to boiling; the calcium hypochlorite is thus transformed into calcium chloride, and the total chlorine estimated as silver chloride. In another part of the filtrate the chlorine of the hypochlorous acid is estimated by Gay-Lussac's chlorometric method. The total lime and other substances are determined by the ordinary methods in a portion of the compound after treatment with ammonia. The following objection is

made to Calvert's method:—"When a solution of hypochlorous acid is heated nearly to boiling, in presence of recently precipitated calcium carbonate, a portion of the carbonate is converted into calcium chloride. In the resulting analysis, therefore, numbers are obtained representing too much calcium chloride, and too little hypochlorous acid. On the other hand the lime is somewhat soluble in the calcium chloride, and consequently in the solution of chloride of lime. This solution always contains an excess of lime, which affects with error the calculation based on the estimation of the lime."

Calvert further treats a given weight of chloride of lime with absolute alcohol, which, according to him, dissolves only the calcium chloride, which is determined in the alcoholic filtrate. The assumption here is, that the hypochlorite remains undissolved on the filter, and that on subsequently treating with water, this hypochlorite can be estimated in the solution. On testing this process, the author could only detect traces of hypochlorite on the filter, which did not surprise him, considering the susceptibility of alcohol to oxidation, and the oxidising power of the chloride of lime. A great part of the hypochlorite is actually converted into calcium chloride.

The following is a comparison of results obtained by the foregoing methods:—

The chloride of lime was found to contain—

By Kolb's method.			By Calvert's method. Precipitation by carbonic acid.			By Calvert's method. Solution in absolute alcohol.		
$CaCl_2O_2$	36·4 ..	Cl 18·2	$CaCl_2O_2$	28·8 ..	Cl 14·4	$CaCl_2O_2$	traces..	Cl traces
$CaCl_2$	30·2 ..	Cl 19·4	$CaCl_2$	39·6 ..	Cl 25·2	$CaCl_2$	35·40 ..	Cl 24·7
		37·6		39·6				24·7

W. S.

Composition of Various Kinds of Glass. By H. Schwarz (Dingl. Polyt. J., ccv, 423—426).

1. *Crystalline glass from Dresden.* From his analyses the author deduces the general formula, $16SiO_2.2Al_2O_3.13RO$, the symbol RO including manganese oxide, lime, magnesia, soda, and potash. This glass is easily fusible; it has a specific gravity varying from 2·656 to 2·660.

2. *Amorphous glass* showed an almost similar composition, viz., $17SiO_2.2Al_2O_3.13RO$. Specific gravity, 2·641—2·648. These glasses contain tolerably large percentages of manganese oxide (5·60—6·30), which renders the glass easily fusible, acting analogously to lead oxide. The author suggests that the manganese residue from chlorine manufactories might be thus made use of. In Weldon's process a compound of manganese and calcium is obtained which might be usefully employed in the glass manufacture.

3. *Venetian Mosaic glass.* The author's analyses of these glasses are unfinished. He gives the composition of one clear blue opaque glass, containing 5·92 per cent. antimony oxide, 9·76 lead oxide, and 1·32 copper oxide. M. M. P. M.

Some Points in the Manufacture of Malleable Iron. By RUSSEL W. DAVENPORT (Amer. Jour. of Science [37], iv, 270—274).

THE samples tested were about ¼ inch thick; they were annealed twice, and analysed before and after each annealing. The conclusions drawn by the author are:—

1. The silicon, phosphorus, and manganese are unaffected by the annealing process.
2. The amount of sulphur is not diminished.
3. The amount of carbon is reduced until almost *nil.*

After the first annealing a black core was noticed running through the mass of iron when fractured; this disappeared after the second treatment: thus the elimination of carbon is gradual, extending from the surface inwards.

Certain annealed samples show a peculiar crystalline structure; the author's analyses do not explain this, but show that it is *not* due to excessive amounts of silicon, phosphorus, or sulphur. Generally silicon may be present in tolerably large quantities, but the smaller the proportion of phosphorus and sulphur, the better is the malleable iron produced.

M. M. P. M.

Production of Spiegeleisen. By D. FORBES (Journal of the Iron and Steel Institute, February, 1872; Dingl. Polyt. J., ccv, 220—226).

SPIEGELEISEN is largely produced in Germany, Russia, and Sweden, and the ores from which it is obtained are of very different and peculiar characters. In Germany it is solely produced from spathic iron ores containing manganese: in Russia from manganese oxides containing iron, and in Sweden by fluxing a mixture of knebelite and manganiferous garnet (combined silicates of iron and manganese). There is one important point to be noticed with reference to these ores, viz., that if the iron and manganese oxides are not in actual combination as carbonates or silicates, they are in a state of very intimate mixture, for whenever pure manganese ores are added to the blast furnace mixture, in the hope of obtaining spiegeleisen rich in manganese, the attempt has been found to be fruitless, or only a small fraction of the added manganese combining with the iron, while the greater portion is carried off in the slag. To produce pig-iron rich in manganese, the manganese must therefore be added to the mixture in the form of a strong compound containing iron; the reduction process is thereby facilitated, since a mixture of the oxides of manganese and iron is more easily reduced to the metallic state, and is thus enabled to unite with the iron of the charge. With manganese alone there is a great tendency for this metal to pass into the slag as a silicate, from which it cannot be profitably recovered. To prevent this, the heat should be as great as possible, and the reducing power of the furnace almost complete. The oxides of manganese are much less easily reduced, and require more time and a much higher temperature than those of iron. In the production of spiegeleisen, the following points should be especially observed:—

1. The manganese ore used should contain a large proportion of iron, in order to secure the easy reduction of as large a portion of manganese.

2. The furnace charge should be basic, *i.e.*, an excess of limestone, or, better, of burnt lime, should be used.

3. The draught of the furnace should be much slower than in the ordinary process, in order to give more time for the reduction of the manganese.

4. The furnace temperature should be as high as possible, the air employed as hot as possible; and as coke bears a stronger pressure of air and developes a greater heat, it is preferred to wood charcoal in this process.

A. Keiller, the director of certain Swedish works, assured the author that he once produced a product which contained 15 p.c. manganese, with only $2\frac{1}{2}$ p.c. carbon, but that this did not possess the well-known appearance of spiegeleisen, and was objected to in the market. He also obtained a pig, which contained 23 p.c. manganese with only 2 p.c. carbon. Mr. Henderson, of Glasgow, further informed the author that "it is a well-known fact that the carbon diminishes in proportion as the manganese increases in the iron alloy, so that with 30 p.c. manganese the carbon sinks down to 0·25 or 0·40 p.c."

In Filipstad, in Sweden, spiegeleisen has been made by using native oxides of manganese, especially Hausmannite, which contains 72 p.c. manganese. The iron produced contained only 4 p.c. manganese, the excess of the metal passing away in the slag.

The ores employed in Germany for the manufacture of spiegeleisen, are found in veins in the Devonian formation, on the east bank of the Rhine. They are spathic ironstones, which consist of carbonate of iron intimately mixed with carbonate of manganese. They further contain more or less copper and iron pyrites, with traces of galena and zinc blende, and frequent occurrence of quartz. Analyses of the products of three different mines are as follows:—

	Stahlberg. p.c.	Kirschenbaum. p.c.	Huth. p.c.
Iron	41·70	42·58	42·21
Manganese	8·16	6·46	8·70

It is proved that the well-known foliated texture of spiegeleisen depends more upon the amount of carbon contained in it than upon the amount of manganese. This structure is also better developed if the iron, after running off, is covered over with slag, so as to allow it to cool more slowly.

The following are analyses showing the percentage composition of spiegeleisen manufactured with coke in Germany.

	C.	Si.	S.	Cu.	Mn.	Fe.
(1)	4·129	0·458	0·015	0·219	8·706	85·929
(2)	5·04	0·41	0·08	0·16	7·57	86·74

W. S.

Mushet's Special Steel. By Fr. Kick (Dingl. Polyt. J., ccv, 488).

Experiments were tried in the author's presence to test the quality of this tungsten-steel. A sample of the steel was prepared with all the necessary precautions, and quite according to Mushet's process, but it would not bear forging. A chisel made from it would not bear the blows, and was splintered. A knife which was forged for a planing machine would not stand nearly so well as a cast-steel knife of exactly the same shape. The steel appeared to possess great natural hardness, and a fine, scaly fracture, but was too brittle.

Prof. Heeren gives an account of this same variety of steel, in which he speaks very highly of its value for planing machines, &c., apparently contradicting the observations made as above by the author.

Analysis of the two samples showed that they differed to some extent in their proportions of tungsten and manganese, that examined by Heeren containing 8·3 p.c. tungsten, and 1·73 manganese, whereas analyses by Gentl and Janowsky of the same experimented upon by the author, gave as a mean, 87·52 iron, 2·53 manganese, 8·78 tungsten, 0·76 silicon, 0·01 phosphorus, 0·02 sulphur, 0·41 carbon, and a trace of titanium.

W. S.

Manganese in Steel. By F. Kessler (Dingl. Polyt. J., ccv, 439).

The percentage of manganese in various steels, determined by the author's method, ranges from 0·438 in one of Krupp's steels, to 0·170 in a steel from Hörd. English steels, said to be free from manganese, showed 0·105 and 0·08 per cent. of this metal.

M. M. P. M.

Electro-Magnetic Deposition of Nickel. By J. M. Merrick, (Chemical News, xxvi, 209).

The author has determined the actual and theoretical amounts of nickel deposited on a slip of platinum, which formed one terminal of a wire connected with a battery of two Grove's cells, the other terminal being a plate of nickel.

Solutions of various nickel salts were employed, and the theoretical amount of nickel was calculated from the amount of hydrogen set free. The value of the solution for plating purposes is thus arrived at.

Sulphate of nickel gave seemingly 10·7 per cent., showing that some oxide was mixed with the metal. *Ammonio-sulphate*, and *ammonio-chloride of nickel* gave 96 per cent. of the theoretical amount. *Nickel-ammonium sulphate* gave 93·5 per cent. The other salts tried gave amounts varying from 10 to 50 per cent.

M. M. P. M.

Recovery of Tin from Tinned Iron Plates.
(Dingl. Polyt. J., ccv, 440—443).

This paper describes a process which depends upon a peculiar form of the apparatus in which hydrochloric acid, mixed with a little nitric acid, is caused to act on the tinned plate, any lead present being precipitated, after evaporation, by sulphuric acid, and the tin then removed by means of zinc.

The solution contains iron and zinc and may be used as a disinfectant, or for the preparation of various colours.

Full details of the apparatus are given in the original paper.

M. M. P. M.

Aluminium Gold-Purple. By H. Schwarz
(Dingl. Polyt. J., ccv, 426).

The author has obtained a clear rose-purple colour upon porcelain, by mixing a soda-solution of alumina with gold chloride. Alumina and gold oxide were precipitated in the finely divided state. This precipitate was dried and burned into porcelain.

M. M. P. M.

White Paint for Metallic Surfaces. By Dr. Sels
(Dingl. Polyt. J., ccv, 490).

Pure, finely-powdered zinc-white (zinc oxide) is mixed with a solution of soda water-glass of 40° to 50° Baumé, to the right consistency for an oil colour. The metallic surface to be painted is well cleaned and washed with hydrochloric acid, and afterwards with water, and the paint is laid on in successive coatings. Not too much paint must be mixed at a time, as it will become thick and dry on standing, on account of chemical combinations setting in. A surface thus painted preserves a dazzling white appearance. By addition of mineral colours various tints may be obtained.

W. S.

Colouring Paraffin and other Materials black for Candle-making. By R. Böttger (Dingl. Polyt. J., ccv, 490).

The materials (wax, stearic acid, paraffin, &c.) are melted, and digested for some minutes with coarsely powdered or bruised anacardium nuts (the fruit of "*Anacardium Orientale*"). This nut contains a black fluid vegetable fat, which combines intimately with the fused candle materials, and does not prejudicially affect the illuminating power of the candles.

W. S.

Preparation of a Black Printing Colour resisting the most powerful Chemical Agents, for Linen and Cotton Fabrics. By R. Böttger (Dingl. Polyt. J., ccv, 491).

The fluid vegetable fat contained in the juice of the anacardium nut may be used to advantage in printing linen and cotton fabrics. By

treatment with acids or alkalis, this colour does not suffer the slightest diminution of intensity; indeed with the latter it gains notably. The coarsely powdered nuts are digested for some time with petroleum spirit in a closed glass at a moderate heat, and the very volatile solvent then allowed to evaporate. The residual syrupy liquid was taken to print with. The tint first obtained on printing is a dusky brownish yellow, changing to deep black when the fabric is wetted with ammonia solution or lime-water. Strong solution of calcium chloride appears to affect the colour slightly, but solution of potassium cyanide, caustic alkalis, and acids of all kinds do not seem to affect it in the slightest degree.

W. S.

Mordanting Woollens with Alum. By R. HARVEY (Dingl. Polyt. J., ccv, 491).

THE object of this paper is to show that in mordanting woollens with alum, a strong solution must be avoided, and that only small quantities of the alum must be used, as with large quantities the alumina hydrate deposited in the fibres is redissolved, and the woollen is thus found not to be so deeply or so easily coloured as when small quantities are employed. The amount of alum recommended by the author is one-tenth of the quantity of woollen to be coloured. He found that even after washing the woollen with weak nitric acid solution, to remove any alkali derived from the soap with which it had been washed, or lime from the water, a decomposition of the alum took place and alumina hydrate was deposited in the fibre of the material. This decomposition of the alum had evidently been effected by the fibre of the woollen itself. Reiman's theory is based upon the view that the alum is split up into its single elements by dialysis.

Basic aluminium sulphate separates in the fibre of the material by the decomposition of the aluminium sulphate of the alum, whilst the excess of acid remains in the water, and in the case of a weak alum solution, is too dilute to effect the solution of the basic sulphate.

W. S.

Use of Phenol in Leather Dressing. By BANDER (Dingl. Polyt. J., ccv, 492).

BY the employment of phenol in solution or diffused as vapour, any damage occurring in the tan-yard, or in the dressing and manufacturing of leather, which is due to decomposition of the animal matter, mouldiness, &c., may be arrested or prevented; the leather is also actually benefited by the application, being rendered softer and more supple.

W. S.

Use of Aniline Colours dissolved in Collodion.
By F. SPRINGMÜHL (Dingl. Polyt. J., ccv, 277).

COLLODION wool is treated in a closed flask with a mixture of 2 vols. ether and 1 vol alcohol of 95 per cent. till a thick but clear solution is obtained. To this ether is added to the desired point of dilution, which must be such that the liquid can be poured on a glass plate, and by inclining the plate can be made to distribute and spread itself thereon. The aniline colour is then dissolved in pure alcohol, the volume of which must be half that of the ether additionally mixed with the collodion. The colour solution is then shaken up with the collodion solution to mix it thoroughly. This collodion lake can be kept as long as desired. When it is poured on glass, a transparent film remains in about two minutes, far exceeding in brilliancy and uniformity the "aniline-lake" coating described in a recent treatise. If the collodion is of the right degree of concentration, the film will adhere tolerably fast to perfectly smooth objects, but most persistently to glass and mica. Paper is beautifully coloured by this lake, but the solution must be as fluid as possible. Beautiful effects may also be produced on photographs, engravings, &c.

W. S.

The Poison-contents of Aniline Colours. By FERD. SPRINGMÜHL (Dingl. Polyt. J., ccv, 174).

SPECIMENS of fuchsine containing from 6·5 per cent. to 0·25 per cent. of arsenic were examined to determine how much of the arsenic was absorbed by the material dyed by the colour. It was found that the quantity of arsenic taken up by wool was far too small to estimate, and that therefore no danger can be incurred by using materials dyed with such aniline colours.

C. H. G.

The New Aniline Colour "Rosa." By Prof. BRONNER (Dingl. Polyt. J., ccv, 172—174).

ITS reactions are:—It is dissolved with a deep-yellow colour by concentrated hydrochloric acid; by great dilution or approximate neutralisation of this yellow liquid with ammonia, the original deep red colour is restored, but disappears on adding an excess of the alkali, a precipitate of calcium arsenate being formed at the same time.

Concentrated sulphuric acid destroys it. Pure nitric acid of 1·28 spec. grav. dissolves it to an orange-yellow liquid which becomes dark red and opaque on warming.

Acetic and lactic acids dissolve it to a carmine-red solution.

Alkalis destroy the colour at ordinary temperatures on standing, or instantly on warming. As chlorine is absent, it appears that the colour consists of arsenate of rosaniline united with calcium arsenate.

C. H. G.

Grenade, a New Dye-stuff. By M. Reiman (Dingl. Polyt. J , ccv, 174).

A brown dye stuff soluble in water, obtained from the residues of the fuchsine manufacture. The mode of preparation is not given.

C. H. G.

Diamond Fuchsine. By W. Fr. Gintl (Chem. Centr., 1872, 442).

The author found in samples of this substance 15, 24·2, and 82·13 per cent. cane sugar. The green metallic-glazing crystals of fuchsine are tolerably easily separated from the sugar if the sample be spread on a sheet of white paper in the sunlight. The sugar crystals are easily recognized by the odour of caramel evolved when they are heated strongly.

M. M. P. M.

New Fuchsine Dye for Cotton. (Dingl. Polyt. J., ccv, 387.)

Ten pounds of cotton-yarn are steeped for several hours in a hot mixture of $1\frac{1}{2}$ lbs. turmeric and $\frac{1}{2}$ lb. good sumach; $\frac{1}{2}$—$\frac{3}{4}$ lb. sulphuric acid are then added, and the yarn is drawn through the solution several times, and washed well. The yellow yarn is now dipped into a warm fuchsine bath; or turmeric with sulphuric acid may be first used, succeeded by immersion in tannin solution, and followed by the fuchsine bath. A beautiful purple colour is produced.

M. M. P. M.

Black Dye for Woollen and Semi-Woollen Goods. (Dingl. Polyt. J., ccv, 387.)

The goods are boiled for an hour and a half with 5 lbs. potassium chromate, 2 lbs. copper sulphate, and 2 lbs. sulphuric acid. After remaining all night they are boiled for an hour with 100 lbs. logwood, 10 lbs. fustic, and 1 liter sal-ammoniac solution. The goods remain again all night, and are then washed with urine.

M. M. P. M.

Violet Dye for Wool. (Dingl. Polyt. J., ccv, 387.)

No particulars are given of the nature of this dye. It comes into commerce under the name of "Violet Exton." Its application to wool seems to be somewhat complicated.

M. M. P. M.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

IX.—*On the formation of Naphthaquinone by the direct Oxidation of Naphthalene.* (Preliminary notice.)

By Charles E. Groves.

Although numerous derivatives of naphthaquinone, such as the chloronaphthaquinones and chloroxynaphthaquinones, have been examined and described, but little attention has hitherto been paid to the quinone itself as compared with anthraquinone; the only notice on the subject that I have been able to find being at the close of a paper published in 1869, by Hermann (*Ann. Chem. Pharm.*, clxi, 88), in which he briefly describes a substance resembling a quinone in its properties, obtained in small quantity as a product of the destructive distillation of potassic chloronaphthosulphoquinonate.

As, from Hermann's description, this method appeared to yield but unsatisfactory results, it seemed probable that the process employed with such success by Græbe and Liebermann, of treating hydrocarbons with a solution of chromic anhydride in glacial acetic acid, for the purpose of converting them directly into their corresponding quinones, might be advantageously tried in this instance. Accordingly a solution of naphthalene in warm glacial acetic acid was treated with an almost saturated solution of chromic anhydride in the same solvent; great heat was evolved, the solution turning green and depositing a green chromium salt on the sides of the vessel. As soon as the reaction was complete, the product was diluted with water, which dissolved the chromium salt, and at the same time produced an orange-coloured precipitate containing the impure naphthaquinone. This, when collected, washed, and dried, was of a deep-yellow colour, and had a strong odour, arising from the naphthalene which had escaped the action of the chromic anhydride. As the naphthaquinone in this precipitate was accompanied by a certain amount of a black tarry matter, from which it was very difficult to separate it by crystallisation, it was found to be advantageous to partially purify it by distillation in the vapour of water, in which it is easily volatile, although not so readily as naphthalene. The long, bright-yellow crystals which adhered to the sides of the condensing tube, consisting almost entirely of naphthaquinone and naphthalene, were either at once purified from the latter by alternate crystallisation from light petroleum oil, carbon bisulphide and alcohol, or the greater part of the naphthalene was

previously removed by allowing the mixture to remain freely exposed to the air for some time in a warm place.

The *naphthaquinone*, as thus prepared, is a bright-yellow crystalline substance, which melts at about 125°, and begins to sublime below 100°. Although but slightly soluble in cold water, it is readily volatile in the vapour of water at 100°, communicating to it a pungent odour, resembling that which is so characteristic of ordinary quinone. It is but slightly soluble in light petroleum oil, readily in benzol, carbon bisulphide, chloroform, and ether, especially when hot, and crystallises by spontaneous evaporation from its solution in the latter in well-formed rhomboidal plates. It is very soluble in boiling alcohol, but crystallises out in great part on cooling. It is soluble in concentrated sulphuric acid, and in glacial acetic acid, being again precipitated on the addition of water. It dissolves in alkalis, forming a reddish-brown solution, in which acids cause a precipitate of a bright-red colour, the nature of which I have not yet examined. When the quinone is boiled with concentrated hydrochloric acid, it is apparently converted into *hydromonochloronaphthaquinone* in a manner similar to that in which hydrochloroquinone is formed from ordinary quinone. The analytical results obtained with naphthaquinone correspond with the formula $C_{10}H_6O_2$.

Hydronaphthaquinone, $C_{10}H_6O_2.H_2$. A cold aqueous solution of sulphurous anhydride is almost without action on naphthaquinone, but when the latter was boiled with strong hydriodic acid and amorphous phosphorus, it dissolved, forming a colourless solution which deposited long needles of the hydronaphthaquinone on cooling. This compound crystallises in colourless needles which melt at about 176° and dissolve with comparative readiness in boiling water, crystallising out again, in great part, on cooling. It is readily soluble in alcohol and ether, even in the cold, also in glacial acetic acid, slightly soluble in hot benzol, crystallising out again on cooling in tufts of colourless needles, and almost insoluble in carbon bisulphide and light petroleum oil. When treated with oxidising agents, such as chromic acid, &c., it is reconverted into the quinone.

On boiling an aqueous solution containing a molecular weight of hydronaphthaquinone with a molecular weight of naphthaquinone, the latter dissolved, yielding a pale-brown solution which, as it cooled, deposited the dark-purple crystalline hydronaphthaquinone, $C_{20}H_{14}O_4$, corresponding to the green hydroquinone of the benzene series. The same purple hydronaphthaquinone was also obtained when naphthaquinone was boiled with amorphous phosphorus and a weak solution of hydriodic acid. It is readily converted, by treatment with strong hydriodic acid, into colourless hydronaphthaquinone on the one hand, and by oxidising agents into naphthaquinone on the other.

As the properties of the quinone prepared by the action of chromic acid on naphthalene appear to differ in many respects from those assigned by Hermann to the substance observed by him, it is possible that they may be isomeric forms. I hope, however, before long to be able to compare these substances, so as to ascertain whether they are identical or merely isomeric, and also to lay before the Society a more detailed account of naphthaquinone and of some of its derivatives, than I have been able to do in this short preliminary notice.

X.—*Researches on the Polymerides of Morphine and their Derivatives.*

By E. Ludwig Mayer of Glasgow, and C. R. A. Wright, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

The experiments detailed in the several papers united together below were originally commenced by us separately, the first named of us examining the action of zinc chloride on morphine, and the other the actions of hydrochloric and sulphuric acids on the same alkaloid; inasmuch, however, as circumstances have prevented one of us from continuing his investigations, and as the products formed by these different reagents exhibit close family relationships, we think it best to amalgamate our results, and publish them conjointly.

I. *On the action of Zinc Chloride on Morphine.*

When zinc chloride solution of such strength as to boil at about 200° is heated to 120°, a strong solution of morphine hydrochloride then dropped in, and the whole kept at 120°- 125° for twenty minutes, a change is produced, inasmuch as the liquid ceases to yield the usual *blue* coloration with ferric chloride, but gives instead a *red* tint with ferric chloride and hydrochloric acid together. When it was poured into water acidulated with hydrochloric acid, a brown amorphous precipitate was obtained on cooling; the filtrate from this gave, on dilution with water, a further amount of amorphous precipitate less coloured than the first; and on standing for some days, crystals formed, fusible at 100° after drying in blotting paper, and solidifying to a crystalline mass; these appeared to be a loose compound of zinc chloride and morphine hydrochloride;* on recrystallisation, crystals containing less zinc we obtained: and, finally, after several recrystallisa-

* Graefinghoff has described (*Jahresbericht*, 1865, 446) a crystalline compound of morphine and zinc chloride, having the formula $C_{34}H_{38}N_2O_6.2ZnCl_2.4H_2O$.

tions ordinary morphine hydrochloride nearly free from zinc was obtained, the quantity of zinc diminishing at each successive recrystallisation. This hydrochloride gave the usual blue colour with ferric chloride, and yielded on analysis numbers agreeing with those required for morphine hydrochloride :—

Found	Carbon	63·10	Hydrogen	6·28	Chlorine	10·84
Calculated..	„	63·46	„	6·22	„	11·04

Up to this point no appreciable quantity of anything different from morphine has been formed; but if the action be allowed to proceed further, tetrapodimorphine ("apomorphine") is formed amounting to 30—40 per cent. of the morphine used: the yield of this base is larger the lower the temperature and the more concentrated the zinc chloride solution, a longer time, however, being required for the conversion. On precipitation of the product with sodium carbonate and treatment with ether, &c., a crystalline hydrochloride was obtained apparently identical in all respects with that produced by the action of hydrochloric acid.

0·4110 gram gave 1·0115 CO_2 and 0·231 H_2O :—

	Calculated.		Found.
C_{68}	816	67·22	67·12
H_{72}	72	5·93	6·24
N_4	56	4·61	—
O_8	128	10·54	—
Cl_4	142	11·70	—
$C_{68}H_{68}N_4O_8.4HCl$ ..	1214	100·00	

When higher temperatures are employed, other products appear to be also formed; thus, after treatment for one hour at 170°, the product obtained, after precipitation with sodium carbonate, treatment with ether, &c., was black and viscid instead of crystalline; this product was digested with animal charcoal, which almost wholly decolorised it, so that a nearly colourless, viscid hydrochloride was obtained after another treatment with sodium carbonate and ether and agitation with hydrochloric acid; a small quantity of flakes formed in the viscid solution; these were separated by a funnel and dissolved in water; on cooling, crystals were obtained, which at first resembled tetrapodimorphine hydrochloride in appearance, but, after standing over sulphuric acid, lost their transparency and communicated a violet tint to water; finally, they became a violet-coloured mass which gave the following numbers :—

0·3576 gram gave 0·8816 CO_2 and 0·2162 of H_2O, which was strongly acid from presence of HCl.

Found	Carbon 67 24	Hydrogen 6 71
Calculated for tetrapodimorphine hydrochloride	„ 67·22	„ 5·93

It hence appears, that this substance is either isomeric with tetrapodimorphine, or actually is that substance contaminated with a small quantity of some foreign body which causes the crystals to become violet. The physiological action of the substance was examined by Dr. Reginald Stocker, careful comparison being made between this sample and a specimen of tetrapodimorphine hydrochloride of known purity; no material difference was noticeable between the two. On the other hand, this substance formed a platinum salt which decomposed slowly *in vacuo*, and more quickly in the air, and turned first green and then black at 100°; pure tetrapodimorphine platino-chloride is much more stable. The small amount of the substance formed prevented a more minute examination of its properties.

The viscid hydrochloride from which these flakes had separated gave the following numbers after drying at 100°:—

0·3056 gram gave 0 6915 CO_2 and 0 1676 H_2O
0·2881 „ „ 0·1868 AgCl
0·2489 „ „ 0·1615 „

	Calculated.		Found.	
C_{34}	408	61·68	61 71	—
H_{39}	39	5·90	6·09	—
N_2	28	4·23	—	—
O_5	80	12·09	—	—
Cl_3	106·5	16·10	16·04	16·06
$C_{34}H_{37}ClN_2O_5.2HCl$	661·5	100·00		

It would hence appear that the base was formed from morphine by the nascent hydrogen chloride produced by the tendency of the zinc chloride to become basic, in accordance with the reaction—

$$C_{34}H_{38}N_4O_6.2HCl + HCl = H_2O + C_{34}H_{37}ClN_2O_5.2HCl,$$

as will be shown hereafter, this base (along with small quantities of others) is formed by the action of hydrochloric acid on morphine at 100°.

It would hence appear that the dehydrating action of zinc chloride is more marked than its polymerising action; in order to see what is the end-product of its action, approximately equal volumes of solid zinc chloride, strong hydrochloric acid, and morphine were heated together in sealed tubes to 180°—220° for 24 hours; no pressure was observed on opening the tubes; on dissolving the product in water (in which it dissolves very slowly) and precipitating by strong hydrochloric acid, a non-crystalline hydrochloride was finally obtained,

insoluble in absolute alcohol, soluble in weak alcohol: this substance much resembled salts of chlorotetramorphine and bromotetramorphine, but had a much darker colour; with nitric acid it gave a dirty-red colour, and with sodium carbonate an amorphous precipitate, almost insoluble in ether; on analysis the following numbers were obtained, from which, together with its properties, it appears evident that the body was the "tetra" polymeride of "apomorphine," and hence that it may fairly be called *octapo-tetramorphine.*

0·2720 gram gave 0·673 CO_2 and 0·160 H_2O
0·2880 " " 0·1380 AgCl.

	Calculated.	Found.
C_{136}	67·22	67·47
H_{144}	5·93	6·54
N_8	4·61	—
O_{16}	10·54	—
Cl_8	11·70	11·85
$C_{136}H_{136}N_8O_{16}.8HCl$ ..	100·00	

The physiological action of this base has been examined by Dr. J. G. Blackley, who finds that it is *destitute of emetic properties;* doses up to 0·13 gram subcutaneously injected into an adult cat produced neither salivation nor vomiting, but simply slight narcotism; the difference between this substance and its isomeride tetrapodimorphine (apomorphine) is very marked.

When a longer exposure to a lower temperature (36—48 hours at 100°) was tried, the resulting product was a compound of zinc chloride and a base (or mixture of bases) belonging to the "tetra" series, but different from octapo-tetramorphine, and apparently containing chlorine: it was not found practicable to remove all the associated zinc by repeated solution in hot water and separation of the hydrochloride by cooling or by addition of strong hydrochloric acid; finally a product was obtained which yielded the following numbers after drying at 100° (the still adherent zinc chloride being carefully estimated and subtracted from the original numbers):—

0·8249 gram gave 1·9352 CO_2 and 0·4836 H_2O
0·2577 " " 0·6043 CO_2 (H_2O lost)
0·3053 " " 0·1518 AgCl
0·2568 " " 0·0320 Cl.

	Calculated.		Found.	
C_{136}	1632	64·34	63·97	63·95
H_{153}	153	6·03	6·51	—
Cl_9	319·5	12·59	12·43	12·46
N_4	112	4·41	—	—
O_{20}	320	12·63	—	—
$C_{136}H_{145}ClN_4O_{20}.8HCl$..	2536·5	100·00		

This product yielded with sodium carbonate a precipitate insoluble in ether and but sparingly soluble in chloroform; assuming it to be a single substance, it may be regarded as formed from the base $C_{34}H_{37}ClN_2O_5.2HCl$ (which, as just shown, is formed by the action of zinc chloride on morphine) by polymerisation and subtraction of the elements of hydrogen chloride:

$$4C_{34}H_{37}ClN_2O_5.2HCl = 3HCl + C_{136}H_{145}ClN_8O_{20},8HCl;$$

a reaction perfectly parallel with others found to take place with other morphine derivatives, as will be shown in a subsequent paper (*vide* page 218).

II. *On the Action of Hydrochloric Acid on Morphine.*

It has been shown by the author, in conjunction with the late A. Matthiessen (*Proc. Roy. Soc.*, xvii, 455 and 460), that when hydrochloric acid acts on morphine in sealed tubes at 140°—150°, "apomorphine" is produced, the same product being also obtainable from codeine by similar treatment; inasmuch, however, as it was further shown (*Proc. Roy. Soc.*, xviii, 83) that other reactions take place intermediately in the latter case, it becomes desirable to examine the intermediate reactions that take place in the case of morphine.

(A.) Morphine was heated in a flask on the water-bath for six hours, with 5—6 times its weight of strong hydrochloric acid, too little product for successful examination being formed by a shorter time of treatment; the liquid being diluted with water, and nearly neutralised with caustic soda, yielded an amorphous white precipitate with sodium carbonate; this precipitate almost wholly dissolved in ether (morphine solutions do not precipitate instantaneously with sodium carbonate; the precipitate, when it does appear, is made up of crystals, and the base is practically insoluble in ether). The ethereal solution agitated with a few drops of hydrochloric acid, yielded a viscid hydrochloride, which refused to crystallise, and gave the following numbers after drying at 100°:—

0·4085 grm. gave 0·9065 CO_2 and 0·229 H_2O.
0·3160 „ 0·2075 AgCl.

(B.) Morphine was treated as in (A) for five hours; the acid liquid was then evaporated on the water-bath in an open basin for four hours more, being nearly dry at the end of that time; finally a hydrochloride precisely resembling (A) was obtained, after precipitation with sodium carbonate and solution in ether, &c.:—

0·337 gram gave 0·739 CO_2 and 0·188 H_2O.
0·3215 „ „ 0·711 „ (H_2O was lost).
0·3565 „ „ 0·244 AgCl.

(C.) Morphine was gently boiled with about 6 parts of hydrochloric acid for four hours, the product being treated as in (A); a precisely similar hydrochloride was obtained—

0·311 grm. gave 0·694 CO_2 and 0·165 H_2O.
0·308 „ 0·212 AgCl.

When the action of the hydrochloric acid is pushed further than the point reached in (C), the precipitate thrown down by sodium carbonate fails to dissolve wholly, or nearly so, in ether; but in each of the three cases A, B, C, the amount of insoluble substance was very small.

The numbers obtained above approximate in each case to the composition of the base described in the previous paper on the action of zinc chloride on morphine, viz., $C_{34}H_{37}ClN_2O_5.2HCl$, which requires

$$C = 61·68 \quad H = 5·90 \quad Cl = 16·10,$$

but the discrepancy is in each case sufficiently marked to indicate that other products are also present; the nearest compositions deducible from the analyses are the following:—

$$\begin{aligned}
&(A.)\ 8C_{34}H_{38}N_2O_6 + 25HCl - 4H_2O\\
&(B.)\ 4C_{34}H_{38}N_2O_6 + 13HCl - 2H_2O\\
&(C.)\ 4C_{34}H_{38}N_2O_6 + 13HCl - 4H_2O,
\end{aligned}$$

which require the following numbers:—

	A.		B.			C.	
	Calculated.	Found.	Calculated.	Found.		Calculated.	Found.
Carbon....	60·44	60·51	60·03	59·79	60·31	60·84	60·85
Hydrogen..	5·94	6·23	5·92	6·20	—	5·85	5·90
Chlorine ..	16·43	16·25	16·98	—	16·94	17·20	17·03

These compositions are those required for mixtures of bases denoted by the formulæ—

$$\begin{aligned}
(A) &= 5\,P + 2\,Q + R\\
(B) &= 3\,P \qquad\quad + R\\
(C) &= P + 2\,Q + R
\end{aligned}$$

where—

$$\begin{aligned}
P &= C_{34}H_{39}ClN_2O_6.2HCl = \text{Morphine} + 3HCl\\
Q &= C_{34}H_{37}ClN_2O_5.2HCl = \text{Morphine} + 3HCl - H_2O\\
R &= C_{34}H_{36}Cl_2N_2O_4.2HCl = \text{Morphine} + 4HCl - 2H_2O
\end{aligned}$$

whence it is considered probable that the following reactions take place:—

$$\underset{\text{Morphine.}}{C_{34}H_{38}N_2O_6.2HCl} + HCl = \underset{\text{Base P.}}{C_{34}H_{39}ClN_2O_6.2HCl}$$

$$\underset{\text{Base P.}}{C_{34}H_{39}ClN_2O_6.2HCl} = H_2O + \underset{\text{Base Q.}}{C_{34}H_{37}ClN_2O_5.2HCl}$$

$$\underset{\text{Base Q.}}{C_{34}H_{37}ClN_2O_5.2HCl} + HCl = H_2O + \underset{\text{Base R.}}{C_{34}H_{36}Cl_2N_2O_4.2HCl}$$

i.e., that the elements of HCl become added on to morphine *previously to* the abstraction of the elements of H_2O, a reaction similar to that already shown to take place in the case of several iodine derivatives. Experiments now in progress indicate that similar results are produced with codeine.

The last formed base (R) is homologous with the "chlorocodide" of Matthiessen and the author, the reactions which express the formation of the two bases from morphine and codeine respectively being precisely similar—

$$\underset{\text{Codeine.}}{C_{36}H_{42}N_2O_6.2HCl} + 2HCl = 2H_2O + \underset{\text{Chlorocodide.}}{C_{36}H_{40}Cl_2N_2O_4.2HCl}$$

$$\underset{\text{Morphine.}}{C_{34}H_{38}N_2O_6.2HCl} + 2HCl = 2H_2O + \underset{\text{Base (R).}}{C_{34}H_{36}Cl_2N_2O_4.2HCl}$$

Inasmuch as "chlorocodide" reproduces ordinary codeine by the action of water, it is evident that no polymerisation has taken place during its formation; and as its formation appears to be *preceded* by the formation of a base homologous with base (P), it is evident that the formula of codeine must be written $C_{36}H_{42}N_2O_6$, instead of the half of this, as formerly, while by analogy morphine must be written $C_{34}H_{38}N_2O_6$.

Base (Q) is no doubt identical with the body of the same composition obtained by the action of zinc chloride on morphine, as described in the previous paper.

(D.) When the action of hydrochloric acid on morphine is pushed further than the point reached in (C), the precipitate thrown down by sodium carbonate fails to dissolve entirely, or nearly so, in ether; considerable quantities of an amorphous insoluble base, much resembling the tetra bases, are produced by gently boiling morphine and 5—6 parts of strong hydrochloric acid for about five hours (boiling point about 208°, rather higher towards the end). The portion soluble in ether yields a crystalline hydrochloride on agitation with hydrochloric acid; these crystals are tetrapodimorphine (apomorphine) hydrochloride—

0·2565 grm. gave 0·633 CO_2 and 0·145 H_2O.
0·1185 „ 0·2905 „ 0·067 „
0·3205 „ 0·1570 AgCl.

	Calculated.		Found.	
C_{68}	816	67·22	67·30	66.83
H_{72}	72	5·93	6·28	6·28
N_4..............	56	4·61	—	—
O_8..	128	10·54	—	—
Cl_4	142	11·70	12·12	
$C_{68}H_{68}N_4O_8.4HCl$..	1214	100·00		

The portion insoluble in ether was dissolved in hydrochloric acid, precipitated by sodium carbonate, and rapidly filtered to remove morphine (which is not immediately precipitated by sodium carbonate, but appears as crystals on standing); this process was repeated, and the final precipitate dissolved in hydrochloric acid, and fractionally precipitated by sodium carbonate to remove colouring matter; the last precipitate dissolved in hydrochloric acid, forming a brownish solution, from which a brownish tar was deposited on evaporation. This was very soluble in water, and was not precipitated by addition of strong hydrochloric acid, differing in this respect from chlorotetramorphine, which in all other respects it much resembles: after drying at 100°—

0·2795 grm. gave 0·6350 CO_2 and 0·163 H_2O.
0·2845 „ 0·1480 AgCl.

	Calculated.	Found
C_{136}	61·70	61·95
H_{162}	6·13	6·48
Cl_{10}	13·45	12·87
N_8..................	4·24	—
O_{24}..................	14·52	—
$C_{136}H_{154}Cl_2N_8O_{24}.8HCl$..	100·00	

Like "apomorphine," this base gave a deep purple colour with ferric chloride. From the *simultaneous* formation of "apomorphine" and this chlorinated tetra base, it appears probable that both are produced by the polymerisation of, and subsequent elimination of the elements of hydrogen chloride from, the above-mentioned bases (P) and (R); thus:—

Base (R). Tetrapodimorphine.

$$2C_{34}H_{36}Cl_2N_2O_4.2HCl = 4HCl + C_{68}H_{68}N_4O_8.4HCl$$

Base (P). New chlorinated tetra base

$$4C_{34}H_{30}ClN_2O_6.2HCl = 2HCl + C_{136}H_{154}Cl_2N_8O_{24}.8HCl$$

This view is corroborated by the circumstance that when the mixture of (P) and (R) obtained in Experiment B was gently boiled with hydrochloric acid for two hours, tetrapodimorphine and this chlorinated tetra base were actually produced in quantity.

In the manufacture of morphine by the Robertson-Gregory process, during the working up of the mother-liquors of the crude morphine hydrochloride, a substance is obtained as an amorphous, brown, pulverulent mass, which appears to have the composition of a much oxidised "base (Q)", or more probably of a tetra polymeride of that base. When dissolved in dilute hydrochloric acid, dirty flakes were thrown down on the addition of stronger acid; purified thus as far as

possible, and dried at 100°, a gummy, amorphous brittle mass was obtained, which gave the following numbers on analysis :—

0·3320 grm. gave 0·5890 CO_2 and 0·146 H_2O.

0·4075 „ 0·2150 AgCl.

	Calculated.		Found.
C_{34}	408	48·71	48·37
H_{39}	39	4·66	4·88
Cl_3	106·5	12·72	13·05
N_2	28	3·34	—
O_{16}	256	30·57	—
$(C_{34}H_{37}ClN_2O_5.2HCl)_n + O_{11} \times n$	837·5	100·00	

Nitric acid and silver nitrate give a dirty red coloration with this body; sodium carbonate throws down a dirty-brown precipitate, insoluble in ether; not improbably, therefore, it belongs to the tetra series, its formula being $C_{136}H_{148}Cl_4N_8O_{20}.8HCl + O_{44}$.

The physiological action of the mixture of bases obtained in Experiment A has been examined by Dr. Reginald Stocker, and found to be utterly different from that of tetrapodimorphine. Doses of from 0·020 to 0·220 gram injected subcutaneously into adult cats, produced in a short time a condition of extreme excitement, almost amounting to frenzy; neither vomiting, nor purging, nor hypnotism was produced in any instance, whether smaller, medium, or larger doses were given; quantities of 0·1 gram and upwards produced ultimately paralysis for some hours; whilst doses of 0·2 gram brought on convulsions, terminating in death. In these instances salivation was noticed as one of the earlier symptoms; this did not occur with doses smaller than 0·2 gram. Evidently, therefore, it is necessary to purify crude apomorphine hydrochloride by repeated recrystallisation before using it in medicine; otherwise the effects of the drug may be complicated by those due to the presence of the other bases P, Q, R: specimens of apomorphine hydrochloride manufactured by Messrs. Macfarlan were found to be quite white and *absolutely pure*.

The difference between the action of morphine and this mixture of bases is much less than that between this mixture and tetrapodimorphine, which circumstance would appear to corroborate the conclusions previously arrived at, viz., that bases (P), (Q), and (R) are derivatives of ordinary or *non-polymerised* morphine, whilst the base formerly termed "apomorphine," is a derivative of a polymeride, dimorphine, and hence may be appropriately termed tetrapo-dimorphine.

Dr. J. G. Blackley has examined the nature of the action of the tetra base, $C_{136}H_{151}Cl_2N_8O_{24}.8HCl$ produced simultaneously with tetrapodimorphine, and finds that it is entirely unlike tetramorphine, no vomiting being produced by doses of 0·05 gram, subcutaneously injected into adult cats; hypersensitiveness and great excitement with salivation are the most marked symptoms.

III. *On the Action of Sulphuric Acid on Morphine.*

By C. R. A. WRIGHT, D.Sc.

By heating morphine sulphate with excess of sulphuric acid to 150°—160°, Arppe obtained (*Ann. Chem. Pharm.*, 55, 96) a brown liquid, which yielded a white precipitate on addition of water; this precipitate dissolved in boiling water acidulated with sulphuric acid, separating again in amorphous flakes as the liquid cooled; after washing with cold water, Arppe obtained the following percentages:—

Carbon	61·12	61·22
Hydrogen	5·58	5·88
Nitrogen............	3·96	
Sulphur	(*a*) 5·86 (*b*) 5·66	(*c*) 3·56 : 2 62

sulphur determination (*a*) being made by oxidising the substance with potassium chlorate and hydrochloric acid; (*b*) by heating with lime and saltpetre; (*c*) by solution in water acidulated with hydrochloric acid, and direct precipitation by barium chloride. From these numbers Arppe deduced the formula ($C = 6$, $O = 8$) $4(C_{35}H_{20}NO_6) + 5SO_3$, which requires—

$$C = 61·4 \; H = 5·8 \; S = 5·8.$$

Laurent and Gerhardt (*Ann. Chim. Phys.*, xxiv, 112) repeated Arppe's experiments, and obtained a body of similar characters, which gave as percentages

$$C = 63·0 \; H = 5·8 \; S = 5·4.$$

Hence these chemists attributed to it the formula $C_{34}H_{36}N_2O_8S$ ($C = 12$, $O = 16$), which would require $C = 64·5$, $H = 5·7$, $S = 5·1$; and considered it to be a kind of amide related to morphine, as sulphamide is to ammonia.

The late A. Matthiessen and the author (*Proc. Roy. Soc.*, xvii, 455), on repeating Arppe's experiments, succeeded in isolating a small quantity of a base soluble in ether and yielding a crystalline hydrochloride, which furnished the "apomorphine" qualitative reactions; and hence concluded that not impossibly the so-called sulphomorphide was impure apomorphine sulphate. No numbers were, however, at that time obtained.

That the body in question is not a kind of amide was rendered probable by Armstrong (*Chem. Soc. J.*, [2], ix, 56), who found that the so-called "sulphonarcotide," of Laurent and Gerhardt (formed from narcotine as sulphomorphide from morphine), was really the sulphate of a narcotine derivative, viz., of dimethyl-nornarcotine.

The results obtained by E. L. Mayer, and detailed in the previous paper, render it probable that "sulphomorphide" might be the sul-

phate, not of ordinary "apomorphine," but of the *tetra-polymeride* termed octapotetramorphine. To throw some light on this subject, the action of sulphuric acid on morphine was carefully examined. The result of the action of this substance on codeine has been shown to be polymerisation without dehydration, bodies of the same percentage composition as codeine being formed, whose reactions and properties lead to the ascription of formulæ respecting double, treble, and quadruple of the formula of codeine.

(A.) Morphine was dissolved in a considerable excess of sulphuric acid diluted with its own bulk of water (morphine, 30 grams; SO_4H_2, 30 cc.'s; H_2O, 30 cc.'s), and the whole kept at 100° in the water-bath for three hours; less time was found to give rise to too little product for successful examination. The acid liquid was largely diluted with water, and nearly neutralised by caustic soda; sodium carbonate then threw down a white amorphous precipitate, which was quickly separated by filtration. On agitation with ether, this precipitate dissolved, and the ethereal solution yielded, on agitation with a few drops of hydrochloric acid, a viscid hydrochloride, which utterly refused to crystallise on standing for weeks over sulphuric acid. (Morphine is not instantaneously precipitated by sodium carbonate, and the base, when it does separate, is in the form of crystals practically insoluble in ether.) After drying at 100° this product gave the following numbers:—

0·3005 gram gave 0·7000 CO_2, and 0·188 H_2O.
0·3815 ,, 0·8840 ,, ,, 0·229.
0·532 ,, 0·2445 AgCl.

(B.) Morphine was treated as in (A) for ten hours, at the end of which time a product was formed, which, on adding sodium carbonate, gave an amorphous precipitate insoluble in ether. This precipitate, dissolved in the least possible quantity of dilute hydrochloric acid, gave a precipitate of flakes on adding stronger acid; these flakes became tarry when heated to 100° while moist, but remained solid at 100°, if previously dried over sulphuric acid.

0·4245 gram of substance obtained thus by fractional precipitation to remove colouring matters, gave 0·1820 AgCl.

0·3885 gram gave 0·9090 CO_2 and 0·228 H_2O.

Both the product obtained in (A) and this substance have the composition of morphine hydrochloride.

	Calculated.		Found. (A.)		(B.)
C_{34}	408	63·46	63·53	63·19	63·81
H_{40}	40	6·22	6·95	6·67	6·52
N_2	28	4·35	—	—	—
O_6	96	14·93	—	—	—
Cl_2	71	11·04	11·37		10·61
$(C_{34}H_{38}N_2O_6.2HCl)_n$	643	100·00			

Product (B) appears to lose a small quantity of HCl at 100°, becoming slightly basic.

Both these bodies yield purple colorations with ferric chloride, and a blood-red tint with nitric acid; their physical and other properties indicate that (A) is the true homologue of tricodeine, while (B) corresponds to tetracodeine. The following names and formulæ may therefore be appropriately bestowed on them:—

Codeine Series.		Morphine Series.	
Codeine......	$C_{36}H_{42}N_2O_6$	Morphine......	$C_{34}H_{38}N_2O_6$
Dicodeine....	$C_{72}H_{84}N_4O_{12}$		
Tricodeine ...	$C_{108}H_{126}N_6O_{18}$	Trimorphine ..	$C_{102}H_{114}N_6O_{18}$
Tetracodeine..	$C_{144}H_{168}N_8O_{24}$	Tetramorphine.	$C_{136}H_{152}N_8O_{24}$

Attempts to obtain the missing polymeride corresponding to dicodeine have as yet proved fruitless; the non-formation of crystals in the viscid trimorphine hydrochloride solution does not prove that there is no dimorphine present, only that the trimorphine is formed in much larger quantity. It is curious that with codeine the reverse is the case, dicodeine being produced to a much larger extent than tricodeine.

(C.) The acid morphine solution employed in (A) and (B) was heated to boiling and allowed to evaporate slowly, until the boiling point rose to 140°, at which temperature a slight smell of sulphur dioxide became perceptible. On pouring the product into water, a substance was obtained, presenting all the properties and appearances of the product obtained by Arppe, the sulphomorphide of Laurent and Gerhardt. After several purifications by dissolving in very dilute hot sulphuric acid, allowing part to separate by cooling, and filtering while still warm. so as to obtain on complete cooling a second batch of deposit much more free from colouring matter, and finally washing copiously with cold water, a perfectly white product was obtained, agreeing in every respect with the description of sulphomorphide. After drying at 100°, the following numbers were obtained:—

0·2885 gram gave 0 649 CO_2 and 0·155 H_2O.

(*a.*) 0 2435 gram heated with potassium chlorate and hydrochloric acid, gave 0·1015 gram of ignited precipitate with barium chloride; but on treating this with hot dilute hydrochloric acid after ignition, only 0 0765 $BaSO_4$ was left, the weight of which did not diminish by another similar treatment.

(*b.*) 0·2705 gram dissolved in hot dilute hydrochloric acid, and precipitated by barium chloride directly, gave 0 086 $BaSO_4$.

These numbers agree fairly with those required for tetramorphine sulphate, the percentage of sulphur being rather below the theoretical amount, indicating that the salt had become slightly basic by the washing with water.

	Calculated.		Found. (a.)	Found. (b.)
C_{136}	1632	61·08	61·33	
H_{160}	160	5·99	5·97	
N_8	112	4·19	—	
O_{40}	640	23·95	—	
S_4	128	4·79	4·31	4·36
$C_{136}H_{152}N_8O_{24}.4H_2SO_4$ ..	2672	100·00		

The percentage of carbon here found is almost exactly that obtained by Arppe (61·12 and 61·22); the variable percentages of sulphur obtained by this chemist may perhaps be explained by the greater or lesser basicity or acidity in the product examined, according to the amount of washing. The apparently larger percentage of sulphur obtained by Arppe on oxidising with potassium chlorate and hydrochloric acid, evidently arose from the precipitation of some other barium salt, besides sulphate (perchlorate?); the above determination (*a*) would indicate 5·72 per cent. of sulphur if the weight of ignited precipitate were reckoned as being wholly $BaSO_4$. Arppe found 5·86 by this process.

Laurent and Gerhardt's analysis was probably made with an insufficiently washed impure product.

From these results it is evident that "sulphomorphide" is not an amide at all, nor has it the composition of *n* morphine + $nH_2SO_4 - 2nH_2O$, as Laurent and Gerhardt's formula would indicate; but that it is simply the sulphate of the "tetra" polymeride of morphine. In order to render the evidence on this point quite conclusive, pure "sulphomorphide" was dissolved in hot dilute hydrochloric acid, and precipitated again by adding excess of cold concentrated hydrochloric acid; the precipitate was similarly treated several times, and finally flakes were obtained exactly resembling the hydrochloride of tetramorphine obtained in (B), and containing no sulphur at all. After drying at 100° for several hours, till constant in weight, the following numbers were obtained:—

0·3495 gram gave 0·8280 CO_2 and 0·201 H_2O.

0·4405 „ „ 0·1740 AgCl.

These numbers indicate that the substance had become basic by long-continued heating to 100°, nearly one-eighth of the HCl being driven off.

	Calculated.	Found.	
C_{136}	1632	64·36	64·62
H_{159}	159	6·27	6·39
N_8	112	4·41	—
O_{24}	384	15·16	—
Cl_7	248·5	9·80	9·77
$C_{136}H_{152}N_8O_{24}.7HCl$ ..	2535·5	100·00	

It is hence manifest that the sulphate of tetramorphine had become transformed into the hydrochloride: the product was found to contain no sulphur.

(D.) The mother-liquors from which the "sulphomorphide" had separated during the purification described in (C), were nearly neutralised by caustic soda, precipitated by sodium carbonate, and exhausted with ether: on shaking up the ethereal extract with a drop of hydrochloric acid, a crystalline hydrochloride was obtained in small quantity (not more than 1·0 or 1·5 per cent. of the morphine used). After recrystallisation and drying at 100°, this gave the following numbers:—

0·2220 gram gave 0·5480 CO_2 and 0·122 H_2O.

	Calculated.	Found.	
C_{68}..............	816	67·22	67·32
H_{72}..............	72	5·93	6·10
N_4..............	56	4·61	—
O_8..............	128	10·54	—
Cl_4..............	142	11·70	—
$C_{68}H_{68}N_4O_8.4HCl$..	1214	100·00	

Dr. Reginald Stocker has examined the physiological action of the above-described morphine polymerides with the following general results:—

Trimorphine.—Doses of from 0·025 to 0·1 gram subcutaneously injected into adult cats produced a state of excitement accompanied with salivation (slight with the smaller doses, but very marked with the larger ones). Hypnotism more or less marked followed the excitement. In each of two experiments, where 0·1 gram was given, the cat gradually sank and died in a few hours, death being preceded by convulsions of a tetanic character; in another case, with the same dose, the cat became slightly hypnotised, but entirely recovered in a few hours.

Tetramorphine.—Doses of from 0·01 to 0·10 gram of the hydrochloride of this base were subcutaneously injected into adult cats; profuse salivation and vomiting were in every instance produced in the course of a few minutes. Dilatation of pupils and cerebral congestion (determined by the ophthalmoscope) were noticed in some experiments.

It is noteworthy that the action of tetramorphine appears to be almost exactly the same as that of diapotetramorphine; both of these bases appear (as far as experiments on cats enable one to form an opinion) to be much more powerful emetics than "apomorphine:" doses of 0·01 gram or less of either of the tetra bases injected into cats produced vomiting in every instance; on the other hand, many

experiments with cats were made with specimens of "apomorphine" hydrochloride prepared in various ways (action on morphine of zinc chloride, of hydrochloric acid at 100°, of the same under pressure at 140°, of sulphuric acid, and of phosphoric acid); in all these cases it was found that vomiting was not produced in a cat with a less dose than 0·025 gram subcutaneously injected; smaller doses than this only produced more or less salivation and excitement: from 0·003 to 0·006 gram is, however, sufficient to produce vomiting in a healthy man.

For the sake of comparison, doses of 0·065 gram of morphine hydrochloride were injected into two cats; some amount of excitement was produced, but no salivation nor vomiting: the pupils were dilated in each case, and cerebral congestion was indicated in one instance by the ophthalmoscope. Contrary to expectation, no marked hypnotism was produced in either case.

It would hence appear that morphine, its non-polymerised derivatives, and trimorphine, are chiefly characterised by producing more or less excitement, sometimes followed by hypnotism; whilst diapotetramorphine, tetramorphine, and tetrapodimorphine (apomorphine) are distinguished by their emetic action, this symptom being produced, in the case of the last substance, only by doses of not less than 0·025 gram (these results referring to the physiological action on *cats*, which in some respects appears not to be comparable with that produced on the human subject). Much further research, however, is needed before any theory can be offered of the connection between the chemical composition and physiological action of these and other analogous bodies; the circumstance that the action of "apomorphine" on cats is by no means the same as that on man, whilst that on rodents is again different, tends to show that experiments made on one class of animal do not necessarily give a clue to the action which the drug used may exert on an animal of another kind.

When trimorphine hydrochloride is dissolved in strong hydrochloric acid, and the whole kept at 100° for eight hours, a change is produced in the substance indicated by the reaction—

$$C_{102}H_{114}N_6O_{18}.6HCl + 2HCl = 2H_2O + C_{103}H_{112}Cl_2N_6O_{16}.6HCl.$$

On diluting the acid liquid with water, neutralising with caustic soda, and precipitating with sodium carbonate, a white precipitate is obtained; this is for the most part soluble in ether; the ethereal solution agitated with a few drops of hydrochloric acid gives a viscid liquid, which wholly refuses to crystallise, and accordingly does not appear to contain any appreciable quantity of "apomorphine." On standing over sulphuric acid, a brittle gum was obtained, which yielded the following numbers after heating to 100°:—

0·3355 gram gave 0·7705 CO_2 and 0·190 H_2O
0·2680 „ „ 0·1540 AgCl.

	Calculated.		Found.
C_{102}	1224	62·26	62·63
H_{118}..................	118	6·00	6·29
Cl_8	284	14·45	14·22
N_6	84	4·27	—
O_{16}	256	13·02	—
$C_{102}H_{112}Cl_2N_6O_{16}.6HCl$ ..	1966	100·00	

The occurrence of this reaction in the substance, which evidently corresponds in the morphine series to the polymeride provisionally viewed as *tricodeine* (*Proc. Roy. Soc.*, xx, 278) in the codeine series, corroborates the view that these substances are actually the threefold polymerides of morphine and codeine respectively; it is noteworthy that the action of hydrochloric acid on tricodeine is simply of a dehydrating character, thus—

$$\overset{\text{Tricodeine.}}{C_{108}H_{126}N_6O_{18}.6HCl} = 6H_2O + C_{108}H_{114}N_6O_{12}.6HCl,$$

whilst that on trimorphine is of an entirely different character, the elements of HCl being added on, as well as those of H_2O subtracted; thus—

$$C_{102}H_{114}N_6O_{18}.6HCl + 2HCl = 2H_2O + C_{102}H_{112}Cl_2N_6O_{16}.6HCl.$$

The non-formation of "apomorphine" which might not improbably have been anticipated from the nature of the reaction with codeine, corroborates, therefore, the view that this base is really a derivative of the missing dimorphine, and that its probable formula is, therefore, the one ascribed to it throughout this paper, viz., that of *tetrapodimorphine*, $C_{68}H_{68}N_4O_8$.

When tetramorphine is gently boiled with several times its weight of hydrochloric acid for five hours, and then evaporated down to dryness on the water-bath, a product is obtained which, after solution in water and fractional precipitation with hydrochloric acid to free it from colouring matters, gave the following numbers:—

0·3080 gram gave 0·7190 CO_2 and 0·190 H_2O
0·3840 „ „ 0·1780 AgCl.

	Calculated.		Found.
C_{136}	1632	63·46	63·66
H_{160}	160	6·22	6·85
N_8................	112	4·35	—
O_{24}................	384	14·93	—
Cl_8................	284	11·04	11·47
$C_{136}H_{152}N_8O_{24}.8HCl$ ..	2572	100·00	

It hence appears that the hydrochloric acid had no action on the tetramorphine. In this respect, therefore, tetramorphine resembles tetracodeine, but differs from diapotetramorphine, which undergoes the following reaction when treated with hydrochloric acid—

$$C_{136}H_{148}N_8O_2.8HCl + 2HCl = 2H_2O + C_{136}H_{146}Cl_2N_8O_{20},8HCl;$$

in physiological action, however, tetramorphine closely resembles diapotetramorphine, and differs considerably from tetracodeine.

IV. *Conclusions.*

The following table exhibits the relations to morphine and its polymerides of the derivatives described in these and previous papers*, such derivatives being actually derived *from morphine as starting point;* as will be shown in a future paper, numerous bodies derived from codeine as starting point also belong to one or other of these series. In designating in brief the relationships which exist between the morphine polymerides and their derivatives, the symbols $\overline{M}$, $\overline{M_2}$, $\overline{M_3}$, $\overline{M_4}$ are applied respectively to morphine, dimorphine (hypothetical), trimorphine, and tetramorphine. Each of these bases forms a hydrochloride (and probably other analogous salts) where the number of equivalents of HCl associated in the salt with the base is equal to the number of nitrogen-symbols in the formula of the base, *i.e.*, two for derivatives from morphine, four for those from dimorphine, six from trimorphine, and eight from tetramorphine.

Another class of base included in the table and designated as the *tetrahydro-series*, is formed by the derivatives obtained by the joint action of hydriodic acid and phosphorus on morphine; these may be all viewed as derived from a hypothetical base related to tetramorphine, and containing H_{16} more in its formula than that substance; or, what amounts to the same thing, from the tetra-polymeride of a base containing H_4 more than morphine, *i.e.*, having the formula $(C_{34}H_{42}N_2O_6)_4 = (\overline{M} + H_4)_4$.

* Matthiessen and Wright, Proc. Roy. Soc., xvii, 455 and 460; xviii, 83. Wright, ditto, xx, 203. Wright, Chem. Soc. Journal [2], x, 652. Meyer and Wright, Chem. Soc. Journal [2], xi, 211.

Name.	Origin.	Formula.	Relation to Morphine or polymerides thereof.
	Mono-Series.		
Morphine	....	$C_{34}H_{38}N_2O_6$	$\overline{M}$
"Base P"	Morphine and hydrochloric acid	$C_{34}H_{39}ClN_2O_6$	$\overline{M} + HCl.$
"Base Q"	Ditto; also morphine and zinc chloride	$C_{34}H_{37}ClN_2O_5$	$\overline{M} + HCl - H_2O$
"Base R"	Morphine and hydrochloric acid (homologous to "chlorocodide")	$C_{34}H_{36}Cl_2N_2O_4$	$M + 2HCl - 2H_2O.$
	Di-Series.		
Dimorphine (hypothetical)	....	$C_{68}H_{76}N_4O_{12}$	$\overline{M}_2.$
"Apomorphine" (tetrapodimorphine)	Morphine and hydrochloric acid Ditto and sulphuric acid Ditto and phosphoric acid Ditto and zinc chloride	$C_{68}H_{68}N_4O_8$	$\overline{M}_2 - 4H_2O.$
	Tri-Series.		
Trimorphine	Morphine and sulphuric acid	$C_{102}H_{114}N_6O_{18}$	$\overline{M}_3$
....	Trimorphine and hydrochloric acid	$C_{102}H_{112}Cl_2N_6O_{16}$	$\overline{M}_3 + 2HCl - 2H_2O.$
	Tetra-Series.		
Tetramorphine	Morphine and sulphuric acid	$C_{136}H_{152}N_8O_{24}$	$\overline{M}_4.$
....	Ditto and hydrochloric acid	$C_{136}H_{154}Cl_2N_8O_{24}$	$\overline{M}_4 + 2HCl.$
Diapotetramorphine	Ditto and phosphoric acid	$C_{136}H_{148}N_8O_{22}$	$\overline{M}_4 - 2H_2O.$
....	Ditto and zinc chloride	$C_{136}H_{145}ClN_8O_{20}$	$\overline{M}_4 + HCl - 4H_2O.$
Octapotetramorphine	Ditto ditto	$C_{136}H_{136}N_8O_{16}$	$\overline{M}_4 - 8H_2O.$
....	Diapotetramorphine and hydrochloric acid	$C_{136}H_{146}Cl_2N_8O_{20}$	$\overline{M}_4 + 2HCl - 4H_2O.$
....	Ditto and hydriodic acid	$C_{136}H_{146}I_2N_8O_{20}$	$\overline{M}_4 + 2HI - 4H_2O.$
	Tetra-hydro-Series.		
Hypothetical tetrapolymeride of $\overline{M} + H_4$	....	$C_{136}H_{168}N_8O_{24}$	$(\overline{M} + H_4)_4.$
..	Morphine, hydriodic acid, and phosphorus	$C_{136}H_{164}I_4N_8O_{20}$	$(\overline{M} + H_4)_4 + 4HI - 4H_2O.$
..	Action of water on above	$C_{136}H_{162}I_2N_8O_{20}$	$(\overline{M} + H_4)_4 + 2HI - 4H_2O.$
..	Further ditto ditto	$C_{136}H_{161}IN_8O_{20}$	$(\overline{M} + H_4)_4 + HI - 4H_2O.$

It is noticeable that all the derivatives of the morphine polymerides can be included in one general formula, viz.:—

$$\overline{M}_x + m\mathrm{HX} - n\mathrm{H_2O},$$

where x stands for 1, 2, 3, or 4 in the mono-, di-, tri-, and tetra-polymerides respectively.

m is either 0, 1, or 2.

X is either Cl or I (not improbably Br, &c.).

And n varies from 0 up to 8.

The "tetra-hydro-series" is expressed by the same formula, if $(\overline{M} + H_4)_4$ be substituted for $\overline{M}_x$.

In a future paper it will be shown that similar or identical formulæ apply to the numerous codeine derivatives hitherto investigated.

In conclusion the authors desire to return most cordial thanks to Messrs. Macfarlan and Co., of Edinburgh, whose great kindness in furnishing gratuitously considerable quantities of pure morphine, has contributed in no slight degree to the success of the experiments undertaken, it being impossible in many cases to obtain a sufficient quantity of derivative for examination without the sacrifice of a large quantity of morphine, the instability of the products necessitating great loss in fractional precipitation, &c., to get rid of oxidised products, colouring matters, &c., simultaneously formed, or produced during the process of extraction.

XI.—*Analysis of the Water of the River Mahanuddy.*

By EDWARD NICHOLSON, Assistant-Surgeon, R.A.

THE *Mahánadi*, or Great River, rises in the Central Provinces, draining a sparsely cultivated forest country, the formation of which is principally trap, basalt, and gneiss, with soils produced by the decomposition of these rocks. After a course of about 500 miles it falls into the Bay of Bengal by numerous mouths. On the promontory at the head of the delta, about 60 miles from the sea, is the town of Cuttack; the town itself is on the southern branch, whilst the main river ($\frac{4}{5}$ of the whole) passes on the north or uninhabited side of the strip of land. On the main river, about three miles below its division, is an arricut, or dam, raising the level for the supply of irrigation canals. This arricut is a mile and a quarter long; in the dry half of the year there are usually only a few inches depth of water on it, whilst in the rainy season the river pours over it in immense volume. 11 feet was the greatest depth on it during 1872. At the end of the rainy season, in the beginning of October, when the water was examined, there were 2 feet of water on the arricut.

The water was of ochrey colour, and quite opaque. After seven

days the cloud of fine silt had subsided, but the water remained semi-opaque for four weeks, the duration of my further stay in Cuttack. From the seventh to the fourteenth day, the permanent silt was found to have diminished by only $7\frac{1}{2}$ per cent.

The following are the results of the analysis :—

a. Mineral Matters in Solution.

Total mineral solids..........	12·00 centigr. per litre.
Deduct permanent silt........	3·43 „ „
	8·57

Treatment with boiling water separated these into—

Insoluble................	6·85 centigr. per litre.
Soluble	1·72 „ „

The radical constituents found were—

Potassium	·137 centigr. per litre.
Sodium	·493 „ „
Magnesium..............	·385 „ „
Calcium	1·314 „ „
Iron....................	·015 „ „
Chlorine	·170 „ „
Sulphuric acid	·090 „ „
Nitric acid	·620 „ „
Phosphoric acid	·060 „ „
Silicic anhydride	2·785 „ „
Oxygen of silicates........	·247 „ „
Carbonic acid	2·253 „ „
	8·569

The hardness of the water, by the soap-test, was 5° centigrade scale (each degree = 1 cgr. per litre of calcium carbonate).

b. Organic Matters.

Twenty-four hours after the water had been taken from the river the clearer part was examined by Messrs. Wanklyn and Chapman's process; also, some of the water having been cleared by the addition of 3 cgr. per litre of aluminium sulphate, the permanganate process was applied. The results were—

Ammonia......................	·003 centigr. per litre.
Albuminoid ammonia............	·018 „ „
Oxygen required for organic matter	·06 „ „

From them I assume the presence of ·48 centigram per litre of organic matter, of which ·18 was albuminoïd. The loss of the total solids by cautious sub-ignition was 1·14 centigrams per litre.

c. Suspended Matters.

Coarse and fine silt, desiccated 24·44 centigr. per litre.
Ditto ditto ignited .. 23·33 " "

Composition (ignited).

	Cgr. per litre.	Percentage.
Silicic anhydride	18·31	78·82
Alumina	2·37	10·25
Ferric oxide (and P_2O_5)	1·43	6·14
Calcium carbonate	·47	2·05
Magnesium carbonate	·52	2·26
	23·10	99·52
Phosphoric acid	·11	·47

Permanent silt deposited in the evaporation with ammonium sulphate, 3·43 centigr. per litre.

Composition.

	Cgr. per litre.	Percentage.
Silicic anhydride	2·71	79·1
Alumina	·26	8·1
Ferric oxide	·18	5·2
Calcium carbonate	·25	7·3
Magnesium carbonate	traces	—
	3·40	99·7

Permanent silt carried down by ferric hydrate and insoluble in dilute hydrochloric acid, 3·18 centigr. per litre.

d. General Observations.

As far as information is available, this water contains less dissolved matters than any other river-water in India. The water of the Ganges contains the next smallest proportion of mineral solids, from 10 to 11 centigrams per litre.

The quantity of nitric acid is much larger than is usual in Indian surface waters (tank-waters).

Except as regards the nitric acid, the composition of this water does not differ from the type of Indian surface waters. We find in them that magnesium silicate is very rarely absent; alkaline silicates are common; a variable proportion of the silicic acid is in the free state, but not so much as in subsoil waters, where it is liberated by the action of nascent nitric acid.

The total amount of silt, 28 centigrams per litre, approaches that estimated by the irrigation engineers in Orissa, to be brought down in floods, viz., 1 cubic inch for each cubic foot of water.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Researches in Actino-Chemistry (Second Memoir). Distribution of Chemical Force in the Spectrum. By J. W. DRAPER (Phil. Mag. [4] xliv, 422—443).

IN a former memoir on the distribution of heat in the spectrum, the author has taken exception to a view which he considers to be generally, if not universally, held, that heat rays are confined, or at least exist chiefly, in the less refrangible parts of the spectrum. In the present communication, he shows that all parts of the spectrum are capable of producing effects of chemical composition and decomposition. He thinks that the curves frequently given in books to show the relative intensities of heat rays and of actinic rays in various parts of the spectrum are misleading. It ought to be explained that the heat curve depends for its form on the material of the prism, and that the actinic curve has been obtained chiefly from experiments with silver compounds.

The points to be established are stated thus:—

"1. That, so far from chemical influences being restricted to the more refrangible rays, every part of the spectrum, visible and invisible,* can give rise to chemical changes, or modify the molecular arrangement of bodies.

"2. That the ray effective in producing chemical or molecular change in any special substance is determined by the absorptive property of that substance."

Mr. Draper considers that the existence of the error which he assumes is partly due to the fact that experiments on the chemical action of light have been chiefly carried on with silver compounds. These are apparently almost solely affected by the more refrangible rays, unless special modes of experimentation are applied to examine whether the other parts of the spectrum have any effect on them or not.

Mr. Draper has examined† the chemical effect of radiations on a great many substances, and comparing the results, he arrives at the conclusions above stated and extended below. The experiments described are on silver compounds, bitumens and resins, carbonic acid produced by plants in sunlight, coloration of flowers, union of chlorine and hydrogen, and the bending of stems of plants in the spectrum.

Silver compounds may themselves be made to show the chemical action of the less refrangible rays of the spectrum. It is of a peculiar

* What the limits assigned to the invisible rays are, is not stated.—J. T. B.

† It does not appear that the paper is intended to describe recent experiments, but rather to consider the subject in a general way.—J. T. B.

kind. The rays of lower refrangibility, instead of having a power of decomposing silver iodide and such compounds, appear to have the power of preventing decomposition. For if a Daguerreotype plate be exposed to the spectrum, while, at the same time, it is receiving diffused light of little intensity, it is found, on exposing it to vapour of mercury, that in the less refrangible parts, except where the *dark lines* of the heat-rays occur, the iodide of silver has been completely protected from the action of the diffused light, and that these dark lines stand out as lights on a dark ground.

The less refrangible rays of the spectrum have even the power of reversing the effect of diffused light on the iodide of silver. A Daguerreotype plate that has been exposed for a short time to weak diffused light, if it be then placed in the camera and exposed to the spectrum, presents precisely the same appearance as that just described for the joint action of the spectrum and a diffused light simultaneously.

Results similar to those just described were obtained with other silver compounds.

When the spectrum is allowed to fall on a plate covered with solution of West Indian bitumen in benzene, and developed by means of a mixture of benzene and alcohol, a complete photograph of the spectrum between the lines A and H is obtained. Every ray in the spectrum appears to act, the only unaffected places being the Fraunhofer dark lines.

To determine what rays effect the decomposition of carbonic acid in presence of chlorophyll, experiments were made, in 1843, as to the place in the spectrum of maximum evolution of oxygen, and also as to the rays that have effect in turning etiolated plants green. It appears that the effective rays are included between the lines B and F, and are thus seen not to be the most refrangible rays of the spectrum.

From experiments of Herschel, in 1842, it appears that all the rays of the spectrum are effective in bleaching colours obtained from flowers, each of the colours having particular rays that are most powerful when applied to it. Thus, if paper be stained yellow by means of the *Corchorus japonica*, it is whitened by the green, blue, indigo and violet rays, while the rose-red of the *Ten-weeks* stock is decolorised by the yellow, orange, and red rays.

The action of light in combining chlorine and hydrogen was examined in 1843. It was shown that every ray in the spectrum is effectual, but that the different rays act with different energy. The maximum is in the indigo; the energy there is 700 times that found in the red part of the spectrum.

The bending of the stems and roots of plants, which have been germinated in darkness, and then brought into the spectrum, has been examined by Dr. Gardiner and by Dutrochet. Their experiments confirm the views which Mr. Draper urges.

Having established that all the rays of the spectrum have chemical power, Mr. Draper brings forward experiments to show the selective absorption which he desires to prove.

He examines carefully the cases of silver compounds and of the combination of chlorine and hydrogen. The experiments seem to have

been made about 1842. Subsequent experiments by Herschel, Foucault and Fizeau, Claudet and Becquerel, confirm the results.

When a silver plate is exposed to vapour of iodine at ordinary temperatures, it tarnishes more or less according to the time of exposure. The stages are well marked by the colours that the plate presents. It is successively (1) lemon-yellow; (2) golden-yellow; (3) red; (4) blue: (5) lavender: (6) metallic; (7) deep yellow; (8) red; (9) green. All these films are sensitive, but in very different degrees. The two yellows, numbered (2) and (7) are the most so; the metallic coloured film is scarcely sensitive at all, and the remaining tints are intermediate in sensitiveness.

It is easy to construct a plate with all these colours on it in bands, by screening successive portions of it during the process of iodising. If a second plate, uniformly coloured yellow, and placed in a camera, be exposed to the light reflected from the first, it is found, on developing both plates with mercury vapour, that the images on it of the various bands correspond inversely in intensity with those on the other plate. That is, the parts that have been affected on the first plate have absorbed the light which would be required to affect the second plate, while the light reflected from the unaffected parts still retains the rays necessary to affect the second plate. Thus the yellow films are sensitive, because they absorb the rays suited for the decomposition of silver iodide; the metallic and blue are unaffected, because they reflect them. Experiments on collodion films, sensitized by nitrate of silver, are also described. A pile of collodion plates showed absorption of the rays effective in decomposing the nitrate of silver, but it appeared that the passage of the ray through one plate or even several was not sufficient to absorb completely all the effective portion of the light from a gas flame.

Experiments with chlorine and hydrogen confirmed the above conclusions. Certain rays alone have power to promote the combination of the two gases, and on examination it was found that these are the rays that are absorbed by chlorine. If a test-tube be filled with hydrogen and chlorine resulting from the decomposition of hydrochloric acid, and placed within a large vessel filled with chlorine gas, it may be exposed with perfect safety to daylight; but on removing the chlorine gas, and substituting atmospheric air in the surrounding vessel, explosion immediately takes place. The chlorine in the surrounding vessel has thus completely sifted the light of the rays that would cause combination. Experiments were also made with a chlorohydrogen actinometer. A mixture of hydrogen and chlorine was tried as an absorber, and it was found that the presence of hydrogen does not increase the power of chlorine for absorbing the rays that would promote the explosion of the mixture in the test-tube. The experiment was tried, not with the test-tube, but with the actinometer mentioned above, and described by the author in the *Philosophical Magazine* for December, 1843.

From these and other experiments Mr. Draper concludes that the whole of the spectrum is capable of producing chemical effects. The particular rays which produce chemical effects in any particular case depend on the nature of the substance exposed to them. The curves

presented in elementary books to indicate distribution of energy capable of producing chemical change he considers to be misleading.

J. T. B.

Fluorescent Relations of Certain Solid Hydrocarbons found in Petroleum Distillates. By HENRY MORTON (Chem. News, xxvi, 272).

IN the distillation of petroleum, there passes over, towards the close of the operation, a thick, brown, tarry matter, from which, by treatment with alcohol and benzene, the author has extracted a solid crystalline hydrocarbon, of greenish-brown colour and pearly lustre. This substance, which he terms "thallene," has attracted attention, more particularly on account of its peculiar fluorescence, which closely resembles that of anthracene, but the crystalline form, solubility, and fusing points of the two bodies differ considerably.

Accompanying the communication are diagrams illustrating the spectra afforded by the fluorescent solid and by its solution in benzene. Diagrams of the two absorption-spectra are also given. In the spectrum of the fluorescent light given by a solution, all the bands are moved towards the more refrangible end of the spectrum, the greatest displacement being observed with an ethereal solution and the least with a solution in carbon sulphide. The bands of the absorption-spectrum are displaced in a similar manner.

If a sunlight spectrum be thrown upon a screen of paper coated with a solution of thallene in ordinary varnish, an intense fluorescence of a rich green colour is excited, upon which the lines of the extra-violet spectrum are seen to great advantage; it is proposed therefore, in order to study this portion of the spectrum, to substitute this hydrocarbon for the peculiar uranium phosphate used by Stokes.

Almost all the reactions obtained with this substance find a parallel in impure anthracene, with which latter substance it also agrees, in the fact that, when its solution is exposed to bright sunlight, it no longer produces absorption-bands. The crystals which separate from a hot solution, after exposure to light, have lost their yellow colour and green fluorescence; they are of a slightly leaden tint, and fluoresce bright blue. The spectrum of this fluorescent light shows an upward displacement of the bands, a little greater than that observed with the solution in ether.

J. W.

Fluorescent Relations of Anthracene and Chrysogen. By HENRY MORTON (Chem. News, xxvi, 199).

THE author has examined the fluorescent light emitted by anthracene in various states of purity, such as the olive-green commercial variety, the light brown, and snow-like powder, and also the pearly scales obtained by frequent crystallisation. If any of these forms be illuminated by a beam of sunlight which is condensed by a lens and also passes through a cell containing solution of ammonio-cupric sulphate, they will emit a fluorescent light, which, when examined by a spectro-

scope, gives a spectrum consisting of four bright bands separated by darker intervals. The first bright band is situated in the red, the second in the yellow, and the two others in the green. The author has, however, prepared some absolutely pure anthracene, which, on examination as above, yielded a pretty blue fluorescence, and in the spectroscope gave a perfectly continuous spectrum. He concludes that this bright band spectrum is due to the presence of chrysogen in the ordinary samples of anthracene. This substance also gives a very characteristic absorption-spectrum, showing two strongly-marked bands, one at F, the other towards G, and a less defined one at G, with a total extinction of all rays at a point slightly beyond G.

If a sample of ordinary commercial anthracene be dissolved in benzene, its solution shows a brilliant green fluorescence, which, on examination with the spectroscope, gives a spectrum of the same character as the solid, with the exception that all the bands are shifted towards the widest end of the spectrum.

A. P.

Colour-Dispersion of Fuchsine. By C. Christiansen (Pogg. Ann., cxlvi, 135).

The following are the indices of refraction found by the author:—

Extreme red.	Yellow.	Blue.	Violet.
1·450	1·516	1·338	1·374

These numbers agree with those found by Kundt (*ibid.*, clxv, 128) for the violet light, but exhibit a much stronger anomalous dispersion, on account of the greater concentration of the liquid used.

H. W.

State of Salts in Solution. By M. Berthelot (Compt. rend., lxxv, 435—439, 480—484, 538—542).

When there is a single equivalent of a given base in presence of an equivalent of each of two or more different acids in the same solution, it is interesting to know what is the real state of the combinations in the solution. By means of a method founded on the distribution of bodies between two liquids, each of which is a solvent for the body in question, but which do not dissolve each other, an examination of the question has already been attempted by M. Berthelot and M. de Saint-Martin (*Ann. Chim. Phys.* [4], xxvii, 433; *Chem. Soc. Journ.*, Jan., 1873). The present experiments make use of the heat given out, or absorbed, on mixing solutions of the bodies to be examined as data from which the state of these bodies in presence of each other may be determined.

The case of monobasic acids is considered first. The experiments are made in the following way:—Solution of sodium acetate, one equivalent in grams dissolved in two litres of water, was mixed with solution of nitric acid, one equivalent in two litres, and the quantity of heat given out during the mixing was determined. Next solution of sodium nitrate, one equivalent in two litres, was mixed with acetic acid

solution of the same strength, and the heat given out was observed. The quantity of heat found as the representative of the chemical combination which takes place was for the first operation + 450 units, and for the second − 60; the total, found by subtracting the second from the first, that is, by adding 60, is 510 units. Comparing this with the difference between the heats developed during the neutralization of weak nitric acid and of weak acetic acid with soda, the number is found to be exactly the same and in favour of the nitric acid combination. Hence it is concluded that when nitric acid and acetic acid in equivalent quantities are present in the same solution and in presence of one equivalent of soda, the nitric acid takes the whole of the soda to itself and the acetic acid remains completely uncombined.

As is the case with nitric acid, hydrochloric acid, in presence of acetic acid and soda, also completely satisfies itself by forming sodium chloride. The heat evolved proves this. The phenomena observed when a bibasic acid and a monobasic acid are together presented to a single base in solution are various, and such is the case when two bibasic acids are simultaneously presented to the same base. Carbonic acid is completely displaced from its combination by nitric, acetic, sulphuric, and tartaric acids. No bicarbonate is formed. Sulphuric acid completely displaces acetic acid from its combination with the alkalis, and during the reaction much heat is given out. Tartaric acid almost completely displaces acetic acid, but during the reaction heat is absorbed. The result is confirmed by the method of two solvents, referred to above, which shows complete conversion of acetates into tartrates.

The reactions of the oxalates and sulphates in presence of nitric and hydrochloric acids are more interesting and more complex than those mentioned above. Here it is found that acid salts are formed and in quantity depending on the amounts of the various bodies present. The quantity of water especially has an important influence on the result. As was pointed out in a former paper, the six bodies in the solution form a kind of equilibrium among themselves. For example, the result of the finished reaction, and consequently the amount of heat given out, depends on the equilibrium due to proper quantities formed of sodium sulphate, sodium bisulphate, free sulphuric acid, sodium nitrate, free nitric acid, and water. M. Berthelot has examined carefully the case of sodium and potassium sulphates in presence of nitric and hydrochloric acids. Tables are given, showing the quantities of heat evolved and absorbed under various circumstances as to quantities of the bodies and quantities of water present.

J. T. B.

On the Determination of the Melting and Solidifying Points of Fats. By Fr. Ruedorff (Pogg. Ann. cxlv, 279—290).

On testing all the usual methods for determining the melting points of fats, the author obtained the most concordant results by covering a thermometer-bulb with a layer of fat, about 3 mm. thick, immersing it in hot water, and observing the temperatures at which the fat began to separate from the bulb and to ascend through the water. Although some fats, and more particularly nutmeg-butter, did not rise from the

thermometer even at temperatures considerably above those at which they are perfectly fluid, the author prefers his method to Wimmel's, to which the same cause of inaccuracy, namely, adhesion to the glass, attaches in a still greater degree.

The solidifying points of some fats were determined by observing the temperatures at which they became solid whilst they were violently agitated; but with the glycerides and some other fats which exhibit a rise of temperature during solidification, it was found best to take as solidifying point that temperature to which the thermometer rises during solidifying, as this maximum temperature appeared to be more constant than the turning-point, which has been determined and given as the natural solidifying point by Wimmel.

The following table exhibits the author's results:—

	Melts at	Solidifies at
	°C.	°C.
Yellow bees-wax	63·4	61·5 62·6 62·3
White bees-wax	61·8	61·6
Paraffin	49·6	49·6
	52·5 to 54	53
	53	52 9
	52·7 to 53·2	52·7
Spermaceti	43·5	43·4
	44·1 to 44·3	44·2
Stearic acid	55·3	55·2
	56·2 to 56·6	55·8
	56·0 to 54·4	55·7
Japan wax	50·4 to 51·0	..
Cacao butter	33·5	..
Nutmeg butter	70 to 80	..
Mutton suet	46·5 to 47·4	32 to 36
Beef suet	43·5 to 45·0	27 to 35

The remarkable phenomenon of a rise of temperature during solidification was also observed in artificial mixtures of fats; for instance, of spermaceti and stearic acid, and of paraffin and stearic acid, and is probably due to the constantly varying composition of the liquid remaining behind during partial solidification. A change in composition as solidification goes on, may possibly also explain the great interval of temperature during which beef and mutton suet pass from the liquid into the solid state.

R. S.

The Specific Heat of Carbon at High Temperatures. By JAMES DEWAR (Phil. Mag. [4], xliv, 461—467).

WITH the idea of approximating by calculation to the boiling point of carbon, Mr. Dewar has made experimental determinations of the specific heat of carbon at high temperatures.

First, a gas-carbon, and also graphite, cocoa-nut charcoal, and diamond was heated in an iron tube in boiling zinc, and being thus at a temperature of about 1040° C., were plunged into a water-calorimeter. The weight of carbon used was generally about four grams; the water and water-equivalent of the calorimeter together amounted to 514·5 grams, and this was raised through about 2·5° C. in the experiment. From the mean of a large number of experiments the specific heat of carbon between 20° C. and 1040° C. was estimated at 0·32.

To determine it at much higher temperatures, a cubical block of lime 2 inches in the side was pierced to the centre with two channels a quarter of an inch wide, and in directions at right angles to each other. Generally only one of the channels passed entirely through the mass. Two powerful oxyhydrogen flames were caused to play into these holes till the interior was at a white heat. The carbon was then placed at the point of meeting of the holes and kept exposed to the oxyhydrogen flame for a considerable time; after which it was allowed to drop from the mass of lime into the calorimeter.

Bunsen has estimated the limit of the temperature of the oxyhydrogen flame under advantageous circumstances at 2800° C. Deville and Debray consider that under ordinary circumstances a temperature not higher than 2500° C. is reached. From experiments on fused platinum dropped into the calorimeter, Mr. Dewar estimates the temperature of his carbon at 2100° C.

The mean specific heat found under these circumstances was 0·42, calculating from the highest result obtained at a temperature supposed to be 2000° C.

Mr. Dewar is of opinion that the *true* specific heat of carbon at this temperature must be at least 0·5. If this be so, carbon at that temperature conforms to the law of Dulong and Petit.

Taking as the specific heat of carbon at high temperatures the number 0·42, Mr. Dewar estimates the boiling point of carbon. He considers the maximum temperature produced during the oxidation of some of the elements and the heat of combustion of carbon; from these and from an estimate of the latent heat of vaporisation and of liquefaction he places the boiling point of carbon, or rather the point of vaporisation of carbon, at 10,000° C. He thinks it would be difficult theoretically to place it higher.

J. T. B.

Compressibility of Hydrogen and Air at High Temperatures. By M. AMAGAT (Compt. rend., lxxv, 479).

THIS paper contains a brief account of experiments made on the compressibility of hydrogen and of common air.

It is generally supposed that the divergence of hydrogen from Boyle's law is at low temperatures in the same direction as that observed in other gases, namely, greater in amount than that which the law indicates; that at a certain temperature it is zero, and at high temperatures in the opposite direction, giving a smaller compressibility. It has also been supposed that all gases would give similar results if they could be tested at temperatures sufficiently high.

If this be the case, it follows that the divergence of hydrogen from this law, which at ordinary temperatures is opposite in direction to that of other gases, ought, as the temperature increases, to keep this direction unchanged, and to increase numerically; and that common air, whose divergence from Boyle's law has been shown by the author of this paper to be zero at 100° C., ought at such a temperature as 250° C. to be reversed in direction.

On experimenting with a new apparatus suggested by M. Regnault, between common temperatures and 320° C., it was found that instead of this being the case, the divergence of hydrogen did not increase, but rather tended to diminish, while the divergence of air from obeying Boyle's law, practically remained equal to nothing up to this temperature.

Hence the author concludes that Boyle's law expresses a limit to which all gases approach in conformity as the temperature rises, and not a mere theoretical statement which is approximately true for each gas at some particular temperature.

J. T. B.

Formation and Decomposition of Formic Acid. By Julius Thomsen (Deut. Chem. Ges. Ber., v, 957—963).

Favre and Silbermann have found the heat of combustion of formic acid to amount to 96,000 heat-units per molecule, that is, to about as much as that of the carbon contained in it. According to this determination the formation of formic acid from sodium hydrate and carbon monoxide, must be attended with an absorption of heat amounting to 21,000 heat-units, instead of a development of heat as in most other cases. In the formation of formic acid from sodium carbonate and carbon monoxide, and from sodium bicarbonate and this gas, the absorption of heat must amount to 34,500 and 38,000 heat-units respectively. Berthelot sees in these numbers an indication of the possession by formic acid of a different constitution from that of the other fatty acids, and seeks to explain the anomaly in a number of ways. Yet the number given by Favre and Silbermann rests, according to them, upon an imperfect experiment, and its deviation from the theoretical number is regarded by them as due to this circumstance.

The author has therefore made a determination of the heat of combustion of formic acid based on the fact that potassium formate in dilute aqueous solution is completely oxidised to carbonate by potassium permanganate. He finds that—

$$(CO_2HKAq,O,\overline{K}Aq) = 72912 \text{ heat-units.}$$

that is, that 72912 heat-units are developed in the oxidation of the formate in the above manner (the symbol $\overline{K}$ stands for KOH).

From this number he calculates the heat of combustion of formic acid as well as the heat evolved in the formation of the acid from its elements:—

$$\begin{array}{rl} \text{Heat-units.} & \\ 147 = & (CO_2H_2,Aq) \\ 13200 = & (CO_2HKAq,\overline{K}Aq) \\ 72912 = & (CO_2HKAq,O,\overline{K}Aq) \\ \hline 86259 & \end{array} \Bigg\} = \Bigg\{ \begin{array}{ll} & \text{Heat-units.} \\ (CO_2H_2,O) & = 60193 \\ (CO_2,2\overline{K}Aq) & = 26066 \\ \hline & 86259 \end{array}$$

This calculation gives 60193 heat-units for the heat developed by the complete oxidation of a molecule of formic acid to water and carbon dioxide, or $(CO_2H_2,O) = 60193$ heat-units, the other numbers being the results of the author's investigations. The number employed by Berthelot, 96000, is therefore about 36000 too great.

In the formation of formic acid from its elements, the heat-modulus (Wármetónung) is calculated to amount to 105124 heat-units:—

$$\begin{array}{ccccccc} (C,H_2,O_2) & + & (CH_2O_2,O) & = & (C,O_2) & + & (H_2,O) \\ 105124 & + & 60193 & = & 96960 & + & 68375 \\ \text{Heat-units.} & & \text{Heat-units.} & & \text{Heat-units.} & & \text{Heat-units.} \end{array}$$

The numbers here employed are those determined by the author, except that of the heat of combustion of carbon into carbon dioxide, which is that given by Favre and Silbermann.

The author then proceeds to show that the formation of the acid from carbon monoxide and water would be accompanied by an evolution of 6607 heat-units; that the formation of sodium formate from carbon monoxide and soda-ley is attended with a development of at least 19954 heat-units; that the formation of the acid from carbon dioxide and hydrogen would likewise be attended with an evolution of heat amounting to 8164 heat-units; that the heat absorbed in the decomposition of formic acid into carbon monoxide and water by sulphuric acid is compensated for by the heat evolved in the union of the sulphuric acid with the water; and that the decomposition at a high temperature of the vapour of formic acid into carbon dioxide and hydrogen, and the rise of temperature that Berthelot has observed to accompany that decomposition, are to be accounted for in a normal manner.

He therefore concludes that formic acid does not present the remarkable anomalies in the heat-phenomena of its formation and decomposition attributed to it by Berthelot.

E. D.

On Temperature Constants. By S. SUBIC (Pogg. Ann., cxlvii, 452—468).—This is the full paper of which an abstract was given in our last volume p. 591).

Observations on Leidenfrost's Phenomenon. By BERGER (Pogg. Ann., cxlvii, 472 and 474).

Development of Heat by the Friction of Liquids against Solids. By O. MASCHKE (Pogg. Ann., cxlvi, 431).

Expansion of Over-heated Vapours. By H. HERWIG (Pogg. Ann., cxlvii, 161—195).

Spectra of Gases in Geissler's Tubes. By A. WÜLLNER (Pogg. Ann., cxlvii, 321—354).

On the Vibrations produced in the Particles of Bodies by the Vibrations of the Ether, and their reaction on the latter, especially with reference to the explanation of Dispersion and its Anomalies. By M. SELLMEIER (Pogg. Ann., cxlv, 399 and 520; cxlvii, 386 and 525).

Spectrum of the Aurora Borealis. By A. v. PETTINGER (Pogg. Ann., cxlvi, 284).

Inorganic Chemistry.

Ozone and Peroxide of Hydrogen. By F. LE BLANC (Compt. rend., lxxv, 537).

THIS paper contains an account of some experiments made in 1854, which agree with those made by A. and P. Thénard (*Compt. rend.*, lxxv, 175, 458; *Chem. Soc. J.*, 921, 977).

Water acidulated with sulphuric acid was electrolysed while the voltameter was kept at $-10°$ C., by means of a freezing mixture. Oxygen, rich in ozone, was obtained at the positive pole. The amount of it was sensibly less than half the volume of the hydrogen given off at the other pole.

An examination of the water in the voltameter showed the presence of peroxide of hydrogen. It appeared to the author, from his experiments, that the formation of the compound is due to the action of ozone on water in the cold.

J. T. B.

Note on Silicic Acid. By C. RAMMELSBERG (Deut. Chem. Ges. Ber., v, 1006).

IT was found that silica which, after a short ignition, dissolves in a boiling solution of potassium or sodium carbonate, loses this property,

either partly or almost entirely, when it is subjected to a more prolonged and stronger ignition. Hence when the silica obtained in analysis is to be dissolved in potassium or sodium carbonate, this operation should be performed before its ignition.

The author has made a series of determinations of the water contained in silica obtained by the decomposition of an alkaline silicate, or of Wollastonite, and finds that this substance, when dried over oil of vitriol, contains 4·5 to 7 per cent. of water, and that when it is dried at 100° to 140°, it retains from 4 to 5·7 per cent. of water. These numbers correspond to hydrates $n SiO_2 + Aq$, in which n lies between 4 and 8. Air-dried silica retains 13 to 36 per cent. of water. The latter of these numbers corresponds to $SiO + 2aq$, and the former to $SiO_2 + Aq$.

T. B.

Amorphous Silicic Acid. By O. MASCHKE (Pogg. Ann., cxlvi, 90—110).

THE author refers at length to his former papers on the same subject, which show that hitherto all attempts to crystallise silicic acid by precipitation from its solutions have failed. He then treats of the neutralisation of alkaline silicates by means of acids, especially sulphuric acid. The result depends on the degree of dilution, temperature, &c. If both liquids are very dilute, the acid may be added to the silicate, or *vice versâ;* but if they are concentrated, the alkaline silicate must be added to the acid, otherwise a gelatinous mass will be formed. In hitting the exact point of neutralisation, it must be remembered that pure silicic acid shows an acid reaction with litmus. In watery solution this acid has no effect on marble; if therefore, in neutralising silicates with an acid, a drop of the solution be brought from time to time on a plate of marble, a very slight corrosion of the latter shows that there is a small excess of the acid, and therefore neutralisation is complete. The appearance, &c., of pure silicic acid is then noted carefully. Dried at different temperatures, this acid gives varying numbers, expressive of the amount of water it contains. The author thus arrives at the following formulæ:—

$$H_2Si_2O_5,\ H_2Si_6O_{13},\ H_6Si_8O_{19},\ H_6Si_{16}O_{35},\ H_6Si_{18}O_{39},\ H_6Si_{20}O_{43},\text{ and } H_6Si_{22}O_{47}.$$

Ignited silicic is not perfectly insoluble in water.

M. M. P. M.

Action of Silica and some Analogous Oxides upon Sodium Carbonate at High Temperatures. By M. MALLARD (Compt. rend., lxxv, 472—74).

THE quantity of carbonic acid expelled on fusing together silica and sodium carbonate tends, for every temperature, to a certain limit, the rate at which the loss increases with the time following a certain law which can be expressed by the equation $y = \frac{ax}{b + x}$, in which $y =$

loss of carbonic acid and x = time. The author explains these observations by assuming that, at the commencement of the reaction, an acid silicate is formed, which decomposes into neutral silicate and silicic acid, which then acts upon more sodium carbonate, until a state of equilibrium is attained between the neutral and acid silicates and the silicic acid. A similar explanation probably applies to the action of titanic acid and of zirconia upon sodium carbonate.

The sesquioxides of aluminium, iron, and boron behave as monobasic acids, since on fusion with sodium carbonate, they furnish immediately and exclusively the compounds $Fe_2O_3.Na_2O$, $Al_2O_3.Na_2O$, and $B_2O_3.3Na_2O$; even the greatest elevation of temperature does not produce any change in these reactions.

The facility with which the compound $Al_2O_3.Na_2O$ is formed, in which the oxygen of the alumina and of the alkaline oxide bear the same ratio to each other as in the numerous class of felspars and amphigenes induces the author to regard these minerals as compounds of $Al_2O_3.NaO$ with excess of silica.

R. S.

On the Devitrification of Glass. By J. Henrivaux (Bull. Soc. Chim. [2], xix, 6—8).

Wieser has lately published analyses of crystallised glass and of the same glass which has not undergone this transformation (p. 986 of last volume). He finds that both contain about the same percentage of silica and lime, but that the crystallised-glass contains six times more potash than the amorphous, whilst the latter contains nearly twice as much more soda as the former. These facts are altogether contradictory to the results obtained of Pelouze, Clémandot, Bontemps, &c., who have shown that the amorphous part always contains more alkali, whilst the crystals are richer in silica and lime. All glassmakers know that by adding even a small quantity of sand to molten glass, crystalline opaque nodules are formed; and further, when glass towards the end of melting shows signs of crystallisation, the manufacturer knows that too much lime has been added. Glass also becomes crystalline when the crucibles are allowed to cool slowly. The author has analysed some of these nodules, and found that their composition is always different from that of the amorphous glass.

C. S.

Action of Phosphorus on Alkaline Solutions of Metals. By A. Oppenheim (Deut. Chem. Ges. Ber., v, 979—981).

When an ammoniacal solution of copper oxide, nickel oxide, silver oxide, or cadmium oxide is heated with phosphorus and a little benzene in a vessel connected with a reversed condenser, dark precipitates are formed, which may be washed with water, alcohol and carbon sulphide, and dried *in vacuo*. The copper precipitate consists chiefly of metallic copper and copper oxide. Nickel gives a black precipitate consisting of a mixture of nickel phosphide and a salt of one of the acids of phosphorus. From the silver solution metallic silver is reduced.

The cadmium solution gives a brown precipitate, of varying composition, which is decomposed by hydrochloric acid with evolution of hydrogen phosphide, and explodes with nitric acid. On heating it in a current of hydrogen, it leaves cadmium phosphide, Ca_3P_2 as a grey crystalline mass with metallic lustre. An ammoniacal solution of zinc oxide is not acted upon by phosphorus, even when heated with it in closed tubes. A solution of lead oxide in caustic potash gave when boiled in the phosphorus, a black precipitate of metallic lead containing only about 0·4 per cent. of P, and from a solution of stannous oxide in potash, a white slimy body separated out.

C. S.

Quick Reduction of Silver from Old Solutions by means of Phosphorus. By J. Krüger (Dingl. Polyt. J., ccvi, 243).

In frequently experimenting with silver salts, a mixture of solution and precipitates is obtained, in which the silver exists in all kinds of combination. When such mixtures are shaken up with an ethereal solution of phosphorus, the solution and the precipitate soon separate, the former being more or less yellow, the latter intensely black. If light-coloured particles are perceived in the precipitate, the quantity of phosphorus solution employed is not sufficient, and more must be added till the precipitate is uniformly black. The precipitate is next filtered, washed, and dried, or placed, while still damp, in a porcelain dish and boiled with potash-solution. Pure metallic silver is thus obtained. If a solid fused mass is required, pure potassium hydrate is fused in a crucible, and to this the dried precipitate is added by small portions.

W. S.

Preparation and Properties of Gold Monochloride. By G. Leuchs (J. p. Chem. [2], vi, 156—159).

The author calls attention to differences in the directions given in text-books for the preparation of this body, and to the unsatisfactory results usually obtained. According to his experiments, when trichloride of gold is heated, the evolution of chlorine does not cease as soon as the whole of the trichloride is converted into monochloride, as usually stated, but may go on till the gold is completely reduced to the metallic state. This result he attributes to the action of moisture in the air, which, being absorbed by the hygroscopic trichloride, decomposes some of the monochloride already formed into metallic gold and trichloride, the moisture again acting upon fresh portions of monochloride, and so on. The author adopts the following process. Trichloride of gold is heated to 200°—300° on a sand-bath, care being taken to crush all lumps and to bring fresh portions of the material constantly in contact with the basin by trituration with a pestle. The evolution of chlorine is very rapid: the liquefied red chloride becomes first brownish-red then dirty-brown, yellowish-brown and dry, afterwards greenish, and ultimately pure yellow. When the mass acquires a greenish colour, the temperature is lowered gradually to 180°. The evolution of chlorine still continues, and the end of the operation can be judged

of only by the changes of colour. As soon as the powder appears of a pure full yellow, it is removed from the sand-bath, triturated till it ceases to smell of chlorine, and at once transferred to close glass vessels. The product, after cooling, is pure yellowish-white.

J. R.

Ferrous Sulphate precipitated by Alcohol. Ammonio-ferrous Sulphate, and Potassio-ferrous Sulphate. By L. Caro (Ann. Chem. Pharm., clxv, 29).

Barckhausen has stated that ferrous sulphate precipitated by alcohol, contains less water of crystallisation than the ordinary substance crystallised from water. The author dissolved 50 grams of the salt in 50 c.c.'s of hot water, added 50 c.c.'s of absolute alcohol, and drained the resulting magma by the Bunsen water-air pump: after washing with alcohol, he obtained numbers agreeing closely with the formula $FeSO_4,7H_2O$. The salt did not alter appreciably by exposure to air at the ordinary temperature for various periods up to one month.

Rheineck has stated that the ferro-potassic and ferro-ammonic sulphates contain only five molecules of water of crystallisation instead of six, as usually considered; the author finds this statement to be incorrect, as in each case he obtained numbers indicating six molecules.

C. R. A. W.

Phosphotungstic Acids. By C. Scheibler (Deut. Chem. Ges. Ber., v, 801).

The so-called sodium bitungstate ($Na_6H_4W_7O_{24} + 12H_2O$), when dissolved in boiling water, together with half its weight of phosphoric acid, and allowed to stand, yields fine crystals of a salt which the author believes to be represented by the formula, $Na_6H_{11}P_2W_6O_{31} + 13H_2O$. The corresponding sparingly soluble barium-salt crystallises in brilliant octohedrons, efflorescent in the air. The acid obtained by decomposing this salt should have the formula, $H_{15}PW_{11}O_{43} + 18H_2O$.

The author has obtained another acid, having the formula, $H_{11}PW_{10}O_{38} + 8H_2O$, by boiling commercial sodium tungstate with phosphoric acid, neutralising the alkaline liquid with hydrochloric acid, precipitating the barium salt and decomposing it. The acid crystallises, apparently in cubes.

These acids, especially the latter, appear to be of importance, on account of their remarkable behaviour with organic bases. In liquids containing $\frac{1}{200,000}$th of strychnine or $\frac{1}{100,000}$th of quinine, for example, they throw down flocculent bulky precipitates, which become denser in the liquid, and may be filtered and washed with acidulated water. The author believes these acids may be advantageously employed as antidotes to the organic bases.

J. R.

The Atomic Weight of Uranium. By C. RAMMELSBERG (Deut. Chem. Ges. Ber., v, 1003—1006).

THIS paper consists of an enquiry into the consequences of Mendeljeff's proposal to double the atomic weight of uranium. If this proposal be adopted, uranium will be classed with chromium, molybdenum, and tungsten; uranous oxide will become UO_2, and will correspond on the one hand with WO_2 and MoO_2, and on the other hand with ThO_2. Uranous chloride will become UCl_4 and it, like WCl_4, $MoCl_4$, and $ThCl_4$ is slightly volatile, somewhat deliquescent, and is decomposed by water. Uranic oxide will be represented as UO_3 or $(UO_2)O$, and will be classed with the acid oxides WO_3, MoO_3 and CrO_3. In these the acid properties diminish as the atomic weights increase; the acid property of UO_3 is, however, sufficiently illustrated by the existence of the compound $R_2U_2O_7$, this being analogous to $K_2Cr_2O_7$. Moreover, the proposed change brings to light the analogy existing between the oxychlorides UO_2Cl_2, WO_2Cl_2, MoO_2Cl_2 and CrO_2Cl_2, and also the correspondence of the double fluorides $K_3UO_2Fl_5$ and $NaUO_2Fl_3 + 4Aq$, with the fluoxytungstates and fluoxymolybdates $R'WO_2Fl_3 + Aq$, $R'_2WO_2Fl_4 + Aq$, $R'MoO_2Fl_3 + Aq$, and $R'_2MoO_2Fl_4 + Aq$. It is pointed out that the supposed analogy between the salts of uranous oxide and those of magnesia does not exist.

The salts of uranic oxide must be regarded as containing the radical $(UO_2)''$; thus the nitrate becomes $(UO_2)''N_2O_6 + 6Aq$, being analogous to the nitrates of magnesium, nickel and cobalt, and the salt $Am_2(UO_2)S_2O_8 + 2Aq$, appears to be isomorphous with the salt $Na_2MgS_2O_8 + 2Aq$. The acetate $(UO_2)''C_4H_6O_4 + 3Aq$ is not isomorphous with the compounds $R''C_4H_6O_4 + 3Aq$, where R = Ba, Cd, Zn, or Pb.

If the proposed change be adopted, the atomic weight of uranium will be represented by a higher number than the atomic weight of any other element.

T. B.

Mineralogical Chemistry.

On the Isomorphism of the Anhydrous Sulphates of the Metals of the Alkaline Earths. By A. ARZRUNI (Deut. Chem. Ges. Ber., v, 1043—1044).

THE angles of native strontium sulphate or *celestine* vary within certain narrow limits. It is generally assumed that this variation is caused by an admixture of isomorphous barium sulphate. The following table, containing the results of the analysis of different specimens of celestine, shows that this mineral does not contain barium sulphate, but a small quantity of calcium sulphate, and also that there does not exist any simple relation between the variation of the angles and the amount of calcium sulphate:—

Locality.	Ratios of Axes.	SO_4.	Sr.	Ca.
Lake Erie	0·76964 : 1 : 1·25506	52·770	46·926	0·157
Ruedersdorf	0·77895 : 1 : 1·27530	52·685	46·715	0·239
Sicily	0·78035 : 1 : 1·28236	52·512	46·812	0·172
Bristol	0·78165 : 1 : 1·28468	52·609	47·206	0·071
Mokkatam (Egypt)	0·78244 : 1 : 1·28415	52·566	47·230	0·269
Pxhow	0·78750 : 1 : 1·28300	52·343	47·126	0·217

The best analytical results were obtained by fusing the mineral with sodium carbonate, treating the solution of the carbonates of strontium and calcium with ammonium sulphate, collecting the strontium sulphate on a filter, and evaporating the filtrate in order to obtain the strontium sulphate remaining in solution. Although this method gave better results than any other, the strontium sulphate which separates on boiling down the solution, always carries a trace of calcium sulphate down with it, whilst the calcium oxalate still retains some strontium, as shown by spectrum analysis. The mineral can also be decomposed by heating it with a solution of ammonium carbonate in closed tubes in a water-bath for 12—18 hours, with the precaution of placing the tubes in a *horizontal* position.

C. S.

Note on an Aventurin Orthoclase found at the Ogden Mine, Sparta Township, Sussex Co., New Jersey. By Prof. Leeds (American Journal of Science [3], iv, 433).

In sinking one of the shafts of this mine, a very beautiful sunstone was found, exhibiting three facile cleavages, parallel to oP, ∞P∞ and ∞P∞, which afforded the cleavage-angles of orthoclase. The colour of the mineral is a delicate flesh-red, due entirely to imbedded crystalline scales of ferric oxide; the orthoclase itself is translucent and quite colourless. Analysis gave (mean)—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	MgO.	K_2O.	Loss by ignition.	
64·81	19·02	0·23	1·26	0·59	14·30	0·26	= 100·47

In an aventurine oligoclase from Tvdestrand in Norway, Scheerer found 0·36 p. c. Fe_2O_3, an extremely small amount of foreign matter being therefore in both cases sufficient to impart to the felspar a brilliant aventurine character.

H. W.

On a Mineral resembling Cyanite in the Rhenish Basalts. By G. vom Rath (Pogg. Ann., cxlvii, 272).

This mineral, called "glance-spar" (Glanzspath), occurs in several localities in the Siebengebirge. Two specimens were examined by the author, one from the basalt of the Weidberg near Heisterbach, the other probably from Unkel. The two were very much alike, forming

straight-fibred groups of prisms, somewhat flattened parallel to one face, which had a nacreous lustre and distinct cleavage. Hardness between that of felspar and that of quartz. Sp. gr. = 3·150 (at 21° C.), therefore considerably below that of cyanite (3·58 –3·68). Quite infusible before the blowpipe. From the Unkel specimen was detached a crystalline fragment which exhibited the characters of a rhombic prism with angles different from those of cyanite. The small cleavage laminæ exhibited brilliant colours under the polarising microscope.

The analysis of the glance-spar, separated as completely as possible from accompanying minerals, gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	
36·7	57·9	4·4	0·7	0·8	= 100·5

The lime and magnesia, together with part of the iron-oxide, are due to admixed augite, and the rest of the iron to magnetic iron-oxide; both of which minerals are shown by the microscope to be mixed with the glance-spar. Replacing these three constituents by their equivalents in alumina, the composition of glance-spar appears to be 36·8 p. c. silica and 63·2 alumina, leading to the formula $Al_2O_3.SiO_2$, which is the same as that of cyanite. Glance-spar has however neither the form nor the specific gravity of cyanite, and must therefore be regarded as exhibiting a new heteromorphous condition of the combination $Al_2O_3.SiO_2$.

H. W.

Two Calcio-sodic Felspars from the Ural. By G. vom Rath (Pogg. Ann., cxlvii, 274—278).

a. Oligoclase from Schaitansk near Mursinsk, where it occurs in clefts in the granite which formerly yielded the well-known red tourmalines. The crystal examined measured 3 or 4 centimeters in its several dimensions; it is terminated at both ends by the cleavage-faces *P*, and exhibits the crystalline faces *T*, *l*, and *M*, the edges of which are much rounded. It is transparent and colourless, which is seldom the case with sodio-calcic felspars, and is more like adularia and some varieties of sanidine, in not exhibiting the twin-striation parallel to the brachydiagonal which is usually seen in triclinic felspars. Sp. gr. 2·642 (at 18°). Loss by ignition 0·38:

SiO_2.	Al_2O_3.	CaO.	MgO.	K_2O.	Na_2O.	
63·83	22·58	3·42	0·06	1·02	8·86	= 99·77

Oxygen-ratio: $(CaO + K_2O,Na_2O) : Al_2O_3 : SiO_2 = 0·985 : 3 : 9·687$. In composition this mineral is more nearly related to the oligoclase from the tourmaline-rock of the Veltlin than to any other of the nine triclinic felspars formerly examined by the author (p. 287 of last volume), and, like the latter, may be regarded as a mixture of 5 pts. by weight of albite and 1 pt. of anorthite.

b. Andesin from the Uvelka mountain near Orenburg: a fragment 7 centimeters long and broad, 2½ centimeters thick, marked on the very perfect cleavage-face *P*, with an extremely fine striation, which, how-

ever, does not cover the whole face. The mineral is fresh, translucent, white, reddish in some parts from admixture of a small quantity of iron-glance. The felspar is intergrown with grey quartz and black mica, the latter being sometimes interlaminated in a peculiar manner parallel to *P*. Sp. gr. 2·654. Loss by ignition 0·33 :—

SiO_2.	Al_2O_3.	Fe_2O_3.	CaO.	K_2O.	Na_2O.	
60·34	24·39	0·18	5·56	0·73	8·44	= 99·64.

Deducting the ferric oxide, which probably belongs to the iron-glance, the oxygen-ratio is 1·025 : 1 : 8·478.

This andesin is most nearly related to that from the melaphyre of Monte Mulatto near Predazzo (p. 288 of last volume), and, like the latter, cannot be exactly represented in composition by a mixture of albite and anorthite. If we start from the proportion of lime and alkalis shown by the analysis, the proportion of silica comes out rather too high for such a mixture; and if, on the other hand, we start from the observed quantity of silica, the calculated quantity of the lime is too great in proportion to that of the soda.

Rammelsberg has lately pointed out that the analysis of every calcio-sodic felspar yields two atomic ratios, namely, that of Al_2 : Si and that of Na : Ca. He designates as normal analyses those in which these two ratios lead to the same result. It is only, however, in about 10 per cent. of the analyses discussed that this condition is exactly fulfilled; in 40 per cent. the two ratios lead to nearly the same proportion of albite and anorthite, while in the remaining 50 per cent. the calculation founded on the ratio Ca : Na leads to a result essentially different from that which is founded on the ratio Al_2 : Si.

The analysis of the Schaitansk felspar gives Al_2 : Si = 1·484, corresponding to a mixture of 5 mol. albite and 2 mol. anorthite, which requires Ca : Na = 1·5. Now the analysis, after conversion of the potash into its equivalent quantity of soda, gives Ca : Na = 1·502, showing that this mineral has the normal constitution of a calcio-sodic felspar.

In the Orenburg mineral, Al_2 : Si = 1·425, corresponding to 5 mol. albite + 4 mol. anorthite, which requires Ca : Na = 1·25, whereas the analysis, after conversion of the potash into the equivalent quantity of soda, gives Ca : Na = 1·290. If, on the other hand, we start from this, the ratio Al_2 : Si becomes = 1 : 4·367. The Orenburg mineral belongs, therefore, to these calcio-sodic felspars in which calculation from the two ratios leads approximately to the same result.

Both these Uralian minerals confirm the theory of Tschermak already noticed (pp. 50, 288, of last volume).

H. W.

Mineralogical Notes. By G. vom Rath (Pogg. Ann., cxlvii, 279—282).

1. *Tridymite.*—This new form of silica has lately been found by Prof. T. Wolf in a trachytic block dug out of a shaft in the volcanic tufa at the foot of the small volcano of Ilaló, near Quito. The substance of

this block (andesite) is very cellular and porous, and the cavities, 2 mm. to 2 cm. in diameter, are filled with small plates of tridymite interspersed and intergrown with hornblende, golden-yellow mica, and a few shining laminæ of iron-glance.

A similar occurrence of tridymite has been discovered in the Siebengebirge, in a lump of scoriaceous porous trachyte from the Stenzelberg. This lump is so porous that the cavities take up more space than the ground-mass itself, their walls being only a few millimeters thick. This ground-mass contains small crystals of a calcio-sodic felspar, together with augite and hornblende. All the cavities (from 1 to 25 mm. in diameter) are thickly lined and partly filled with tridymite, associated with small octohedrons of magnetic iron ore. Considering the thinness of the walls of the cavities and the small proportion of silica which they contain, it seems most probable that the silica from which this large quantity of tridymite has been formed was not derived from these walls, but from siliceous solutions or vapours saturating the mass and penetrating into its inmost cavities.

Tridymite, which has for some time been vainly sought for in the volcanic region of Naples, *e.g.*, in the rocks of Ischia, Cumæ and Monte Olibano, has at length been found in some blocks ejected from Vesuvius in the eruption of 1822. The substance of these blocks is a fine-grained mixture of sanidine, garnet, and augite, and they contain numerous cavities lined with crystals of sanidine and garnet. On the sanidine crystals are implanted spherical nodules made up of very small laminæ, which exhibit before the blowpipe the characters of tridymite. These tridymite crystals were observed twenty years ago by Scacchi, who, however, mistook them for felspar.

2. *Quartz* has been found, together with iron-glance, in the clefts of a trachytic lava from Lipari, in small crystals, exhibiting all the marks of volcanic sublimation. The iron-glance forms needles ½ mm. thick and 10 mm. long, united in twins, or rather in rows of twins.

3. *Nepheline*, though very widely distributed, rarely occurs in druses distinctly crystallised. It has, however, been found in small but distinct crystals (hexagonal prisms with the basal face) in the trachyte of the Lorberg, which belongs to the sanidine-oligoclase trachytes, or the so-called Drachenfels variety. This is the fourth instance of the occurrence of nepheline in the volcanic district of the Lower Rhine, the other three being (1.) in the sanidine blocks of Laach; (2.) in the lava of Mayen, Niedermendig, and Herrchenberg; (3.) in the dolerite of the Lowenburg.

H. W.

On the Chemical Formula of Epidote. By C. Ludwig (Ann. Chem. Pharm., clxv, 217–228).

Rammelsberg in his "Mineralchemie" (pp. 750–760) gives for epidote the formula $Si_9Al_4Ca_6O_{30}$ or $3(2CaO.SiO_2) + 2(Al_2O_3.3SiO_2)$ —the alumina being more or less replaced by ferric oxide—and has lately endeavoured to support it by the results of an analysis of the epidote of Sulzbach (*Zeitschr. der deutschen geol. Gesellschaft*, 1872, 69); Tschermak, on the other hand, in his well-known memoir on felspars

(*Wien. Akad. Ber.*, l, 585), first represented the composition of this mineral by the formula $Si_6Al_6Ca_4H_2O_{26}$ or $CaO.H_2O + 3(CaO.SiO_2 + Al_2O_3.SiO_2)$; and Kenngott, by careful calculation and comparison of all previously known analyses of epidote, has arrived at the same formula (*Chem. Soc. J.*, 1871, p. 1172).

To decide between these two formulæ the following investigation was undertaken, the analyses being made on perfectly pure specimens of epidote, free from foreign enclosed minerals, as it occurs in the beautiful transparent crystals from Sulzbach.

This epidote contains silica, alumina, ferric oxide, ferrous oxide, lime, water, and traces of manganous oxide, magnesia, and chlorine.

The quantitative analysis was carried out by the processes usually adopted for silicates, excepting that the ferrous oxide was determined by decomposing the mineral with sulphuric acid in a sealed glass tube, and acting upon it with a standard solution of dilute potassium permanganate.

Especial care was bestowed on the estimation of the water, as it is chiefly on this point that previous analyses are at variance. Epidote loses about 0·25 per cent. of its weight by ignition in a platinum crucible over a Bunsen's burner, and nearly 2 per cent. when heated in a gas-flame fed by a blast of air; after this strong ignition it is reduced to a sintered mass easily attacked by acids. To avoid errors which might arise from reduction of ferric to ferrous oxide by the flame-gases, and obtain a direct demonstration of the presence of water in epidote, the mineral previously dried at 150° was enclosed, in Ludwig's experiments, in a platinum tube through which a slow stream of dry air was passed, and heated to whiteness over a gas-flame urged by a blast, the water evolved being condensed in a calcium chloride tube connected with the platinum tube. The mean of eleven experiments made in this manner gave from 1·78 to 2·35 per cent. of water, the mean being 2·05.

The mean result of several analyses of the mineral is as follows:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	H_2O.	MnO, MgO, Cl.	
37·83	22·63	14·02	0·93	23·27	2·05	traces	= 100·73

Or,

Si.	Al.	Fe as Fe_2O_3	Fe as FeO.	Ca.	H.	O.
17·65	12·06	9·81	0·72	16·62	0·23	43·64

The atomic proportions of the elements are therefore—

	Si.	Al.	Fe as Fe_2O_3.	Fe as FeO.	Ca.	H.	O.
	0·630	0·410	0·175	0·013	0·415	0·230	2·727
		0·615		0·428			
Or,	6	5·36		4·07		2·2	25·97

Tchermak and Kenngott's formula requires—

Si.	Al. + Fe as Fe_2O_3	Fe as FeO + Ca.	H.	O.
6	6	4	2	26

The result of the analysis of perfectly pure epidote is therefore to confirm the formula $Si_6Al_6Ca_4H_2O_{26}$.

Epidotes may accordingly be regarded as mixtures of two isomorphous constituents, $Si_6Al_6Ca_4H_2O_{26}$ (aluminium epidote), and $Si_6Fe_6Ca_4H_2O_{26}$ (iron epidote).

The percentage composition of these two varieties in the pure state is as follows:—

	Aluminium epidote.	Iron epidote.
Silica	39·543	33·272
Alumina..........	33·875	—
Ferric oxide	—	44·362
Lime	24·605	20·702
Water............	1·977	1·664

The original paper contains a table of the percentage composition of such mixtures calculated for 1, 2, 3 . . . . . . up to 45 per cent. of iron-epidote, and a comparison of these calculated numbers with all the actual analyses of epidote hitherto published,—excluding however as inaccurate those which take no account of the water, and in which nevertheless the sum of the other constituents is equal to or greater than 100,—also those which indicate a considerable amount of magnesia or alkalis, these having been made upon impure material.

The result of this comparison is to show that the older analyses of epidote also lead to the formula $Si_6Al_6Ca_4H_2O_{26}$, as indeed Kenngott has already shown by a different mode of calculation.

Epidote from the Untersulzbach Valley, in Salzburg (sp. gr. 3·51), has also been analysed by F. Kottal, in Lieben's laboratory, with the following mean results:—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H_2O.	
37·00	22·10	13·80	0·33	25·15	0·03	0·26	= 98·67

These numbers do not differ much from those obtained by Ludwig, excepting in the water, which was determined by igniting the substance, previously dried at 100°, in a stream of carbon dioxide. Probably the degree of heat applied was not sufficient to expel the whole of the water (*Ann. Chem. Pharm.*, clxv, 360).

H. W.

Pucherite. By A. Frenzel (Jahrbuch f. Mineralogie, 1872, 514).

The following observations are supplementary to the author's former description of this mineral (last volume, p. 131):—

Besides the forms ∞P, oP, P∞, and *m*P*n* previously mentioned, there have been observed a pyramid of the principal series as well as the macrodiagonal and brachydiagonal pair of faces, the two latter forms, however, only in very narrow strips. The pyramid occurs chiefly on the thick tabular crystals. Twins are also found.

The colour of the mineral is not only reddish-brown to brownish-red,

but limpid yellowish-brown, hyacinth-red, and dark brownish-black modifications are also found. Streak-powder, always ochre-yellow. Sp. gr. (allowance being made for adhering quartz) = 6·249.

Part of the vanadic oxide in the mineral is replaced by arsenic and phosphoric oxides, its composition being

Bi_2O_3.	V_2O_5.	As_2O_5.	P_2O_5.	
72·16	22·19	3·66	1·34	= 199·35

H. W.

Analysis of Syngenite, a New Mineral from Kalusz in Gallicia. By H. Völker (Ann. Chem. Pharm., clxv, 358).

This mineral was found by Zepharovich in fine crystals on the sylvine druses of Kalusz.* Analysis of substance dried at 100°—

CaO.	MgO.	K_2O.	SO_3.	H_2O.	
16·97	0·46	28·03	49·04	5·81	= 100·31,

leading to the formula $CaSO_4 . K_2SO_4 + H_2O$, and showing that the mineral is closely allied to polyhalite, for which it was at first mistaken. If indeed in the formula of polyhalite, $2CaSO_4 . MgSO_4.K_2SO_4 + 2H_2O$, the $MgSO_4$ be replaced by K_2SO_4 and the whole divided by 2, we obtain the formula of syngenite.

H. W.

Analysis of a Furnace-product containing Magnetic Iron Oxide. By H. Völker (Ann. Chem. Pharm., clxv, 356).

This mineral was found in a cleft of the hearth-stone (consisting of quartz and clay) of the coke-fed blast-furnace of Prevuli in Carinthia, and has doubtless been formed there. It consists of fine steel-grey closely intergrown crystals, strongly magnetic and having a sp. gr. of 5·63. Qualitative analysis showed that it consists of ferrous and ferric oxide, with traces of manganese and of silica or an insoluble silicate. The quantity of ferrous oxide was determined by dissolving the mineral in hydrochloric acid, and titrating with permanganate; the ferric oxide, both by difference, and directly by heating a portion of the solution in a closed flask with hydrochloric acid and potassium iodide, whereby iodine is set free in the proportion of 2 at. I to 1 mol. Fe_2O_3—

$$Fe_2O_3 + 6HCl + 6KI = 2FeI_2 + 3H_2O + 6KCl + I_2,$$

and estimating the free iodine by Bunsen's method.

The mineral was thus found to contain 76·2 p.c. Fe and 23·8 O, or 79·83 FeO and 20·11 Fe_2O_3.

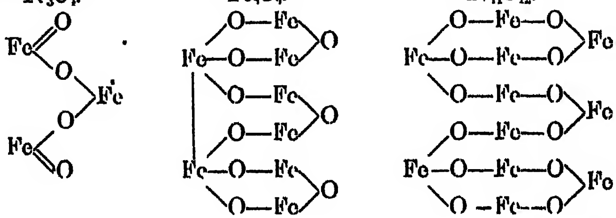
Lieben in a note to this paper observes that the occurrence of crystallised magnetic iron oxide as a furnace-product has often been noticed before, but that such products have hitherto been found to

* The physical and crystallographic characters of the mineral are described by Zepharovich in the June number of *Lotos*, 1872.

agree in composition with the natural mineral Fe_3O_4, or $FeO.Fe_2O_3$. The product above described differs, however, both from this and from the common scale-oxide (generally regarded as $Fe_8O_9 = 6FeO.Fe_2O_3$, or by some chemists as $Fe_6O_7 = 4FeO.Fe_2O_3$), its specific gravity being higher, and its composition agreeing with the formula $Fe_{11}O_{12}$ or $9FeO.Fe_2O_3$.

The constitution of these three varieties of ferroso-ferric oxide may perhaps be represented by the following formulæ:—

Magnetic iron ore, Fe_3O_4. Scale oxide, Fe_8O_9. Furnace product, $Fe_{11}O_{12}$.



H. W.

On a Meteoric Iron lately found in El Dorado County, California. By C. U. SHEPARD (American Journal of Science [3], iii, 438).

THIS mass of iron, weighing 85 pounds, was found in a field. Its surface shows the indentations common to these bodies, the crust or coating being partially oxidised. Turnings taken from it exhibit a sp. gr. of 7·80, which is perhaps a little above that of the mass, owing to slight condensation in the act of separation.

The fragments examined were free from sulphur. A single analysis made on a gram of material gave 88·02 p.c. iron, 8·88 nickel, and 3·50 of insoluble matter, consisting of a mixture of ferrous and ferric oxides, with minute silvery particles of supposed metallic phosphides (schreibersite) = 100·40.

The amount of material at command was too small to allow of search for the other metals usually found in meteoric iron.

H. W.

On a Meteorite which fell at Ibbenbühren, in Westphalia. By S. VOM RATH (Pogg. Ann., cxlvi, 463—475).

THIS meteorite fell on the 17th of June, 1870. Its fall was witnessed by a peasant, who two days afterwards found it buried in a pathway, 7 decimeters below the surface. Before reaching the ground, one end of the stone had split off, and a fragment of the detached portion, weighing 30 grams, was found some 300 yards away.

The general form of the meteorite is that of a flattened spheroïd. Its dimensions are: length, 0·125; breadth, 0·112; thickness, 0·093 meter: probable length before fracture, 0·130 meter. The exterior of

the stone consists of a black layer, scarcely 0·1 mm. thick, which is not smooth and even, but covered with a number of extremely fine fused granulations. When examined with a magnifying glass, the surface exhibits innumerable branching cracks, which penetrate into the interior of the stone, and are filled with the fused mass of the exterior. Inside, the meteorite is much lighter in colour than meteorites generally. It consists of a greyish-white mass, interspersed with a very large number of irregularly distributed crystalline granules of a light yellowish-green colour, some imperceptibly small, others of considerable size, and mostly several millimeters in length. These crystals belong to the rhombic system, but it has not been found possible to determine their exact form. Their mean specific gravity is 3·426. An analysis of them gave the following result—

SiO_2.	FeO.	MnO.	MgO.	CaO.	Al_2O_3.
54·51	17·53	0·29	26·43	1·04	1·26 = 101·06,

showing that the crystals are bronzite, with a large proportion of iron.

The mass of the meteorite, in which the crystals are embedded, is finely granular, white or light grey, and very brittle. Its specific gravity is 3·404. Two analyses of it show that it is almost identical in composition with the crystals of bronzite contained in it.

The Ibbenbühren meteorite is remarkable for the simplicity of its constitution, consisting as it does almost entirely of a single silicate, bronzite. It contains no chrome-iron ore, which is almost always present in meteorites, and no trace of any sulphur-compound. Traces of metallic iron, however, appear to be present. The surface of the meteorite is distinctly attracted by the magnet, a portion of the ferrous oxide of the bronzite having been converted into magnetic oxide by the combined action of the oxygen of the air and a high temperature. At present only three other meteorites of similar constitution are known: the Chassigny meteorite, consisting of olivine; the Bishopsville, of enstatite; and that which fell at Manegaum, in Hindostan, in 1843, and consists, like the present, almost entirely of bronzite.

J. R.

Unusual Amount of Ammonia in a so-called Spa Water.

By C. A. Cameron (Chem. News, xxvii, 6).

A spring situated at Portobello, a suburb of Dublin, has been for many years in some repute as a sulphur spa, and wonderful cures have been attributed to the use of its waters. An imperial gallon contains—solid matters (chiefly calcium carbonate), 24·236 grains; chlorine, 1·11 grains; organic nitrogen, 0·0035 grain; organic carbon, 1·26 grains; ammonia, 0·562 grain; hydrogen sulphide (all, except a trace, combined with ammonia), 0·406 grain; nitrites and nitrates, faint traces. Five gallons evaporated nearly to dryness gave a remarkable jelly-like residue. The water is clear, of a very light yellowish green colour, and has an odour of sulphuretted hydrogen, which passes away after an hour or two. Only minute quantities of iron and silica are present, and there are no sulphides, except the ammonium sulphide.

There is nothing in the water to account for its reputed medicinal qualities; but the enormous amount of ammonia which it contains, when compared with the minute quantity of albuminoid nitrogen, is very remarkable.

Contribution to the Theory of Twin-crystals. By E. Reusch (Pogg. Ann., cxlvii, 569—590).

Contributions to Micromineralogy. By A. v. Lasaulx (Pogg. Ann., cxlvii, 283—307).

Crystallographic Description of Anorthite. By G. vom Rath (Pogg. Ann., cxlvii, 22—63).

Appearances produced in Calcspar by Pressure. By E. Reusch (Pogg. Ann., cxlvii, 307—311).

On the Corundum Region of North Carolina and Georgia, with descriptions of Two Gigantic Crystals of that Species (continuation). (Amer. J. of Sci. [3], iv, 175).

Description of a Crystal of Andalusite from Delaware County, Pennsylvania. By James D. Dana (Amer. J. of Sci. [3], iv, 473).

On the Quartzite, Limestone, and Associated Rocks of the Vicinity of Great Barrington, Mass. By James D. Dana (Amer. J. of Sci. [3], iv, 362, 450).

Organic Chemistry.

The Law of Boiling Points of Homologous Organic Compounds. By Is. Pierre and E. Puchot (Compt. rend., lxxv, 1440—1445).

It is generally held that, in the case of a series of organic compounds, the formulæ of whose terms differ by the constant addition of the molecular group CH_2, there exists between the boiling points of the several terms a constant difference of temperature. The amount of this difference is estimated sometimes at 22° C., sometimes at 21°, or 20°, or even 19°.

This law is made use of as a direction in rectifying or isolating bodies but little known. Nevertheless, the authors are of opinion that it cannot be held as a really exact law, and, having in hand a large number of organic products in a pure state and relatively in considerable quantity, the result of researches on the alcohols of fermentation, they have examined the boiling points of these products with a view to determine how far it holds true.

Ten series of compounds were examined, and the boiling points of 40 substances were determined, and are given in the paper. Some of them are slightly different from those given in the tables in Miller's Chemistry, vol. iii, p. 943 (4th Edition); and some additional numbers are given. As far as the law is concerned, the results may be summed up as follow:—

The series examined were: (i) Monatomic alcohols, 5 terms; (ii) Methyl chloride series, 4 terms; (iii) Bromides, 4 terms; (iv) Iodides, 4 terms; (v) Acetates, 4 terms; (vi) Propionates, 3 terms; (vii) Butyrates, 5 terms; (viii) Valerates, 4 terms; (ix) The aldehydes of the same, 4 terms; (x) Acids, 3 terms, beginning with propionic acid. The following table shows the mean difference between the boiling points of the several terms per addition of CH_2 in the formula, and the greatest departure from the mean, per cent. of the mean, that is exhibited in the series.

Series.	Mean of differences per CH_2.	Greatest departure exhibited per cent. of mean.
I.	16·55	− 39·5
II	30·3	− 25·7
III.	25·8	− 28·2
IV.	26·2	± 31·6
V	19·2	+ 56·2
VI.	17·85	− 40·6
VII	19·2	− 24·5
VIII	18·2	+ 18·1
IX.	25·2	− 37·2
X	18·25	± 23·3

Among the means themselves it will be seen that great differences are found. The results here given show that the law is far from holding in the cases here examined.

On examining the particulars of the numbers obtained, a fact worth noticing presents itself, viz., that the difference between the boiling temperature of the propylic and butylic terms in each series is less than the difference between any other two succeeding terms in the same series.*

J. T. B.

On Several Groups of Isomeric Bodies derived from the Fermentation Alcohols. By Is. Pierre and Ed. Puchot (Compt. rend., lxxv, 1594—1602).

The aldehyde, $C_nH_{2n}O$, derived from a monatomic alcohol, $C_nH_{2n+2}O$, is isomeric with the compound either, $\left.\begin{matrix}C_nH_{2n-1}O\\C_nH_{2n+1}\end{matrix}\right\}O$, which may be considered as resulting from the union of the ether belonging to the same alcohol with the corresponding acid anhydride.

* This is just what may be expected to follow from the fact that the propyl alcohol of fermentation is a normal alcohol, whereas all the other fermentation alcohols are iso-alcohols; but the difference between these two classes of alcohols appears to be disregarded by the authors in all their papers. (See note to the following abstract.)—Ed.

It is also isomeric with the acid derived from the alcohol $C_{2n}H_{4n+2}O$.

An example of this double isomerism is furnished by acetic aldehyde, ethyl acetate, and butyric acid.

Similarly a simple ether of the form $(C_nH_{2n+1})_2O$ is isomeric with an alcohol of the form $C_{2n}H_{4n+2}O$. Ethyl ether, for example, is isomeric with butyl alcohol, methyl ether with ethyl alcohol.

But in all these cases the different members of these groups resemble each other only in composition, without exhibiting, in any respect, a corresponding agreement in properties.

By the mutual reaction of a monatomic alcohol and an acid derived from another monatomic alcohol, two distinct compound ethers may be obtained according as the first alcohol is employed with the acid derived from the second, or *vice versâ*.

These two ethers are isomeric with each other, and may be represented by the formulæ

$$\left.\begin{matrix} C_nH_{2n-1}O \\ C_pH_{2p+1} \end{matrix}\right\} O, \quad \text{and} \quad \left.\begin{matrix} C_pH_{2p-1}O \\ C_nH_{2n+1} \end{matrix}\right\} O.$$

The name *reciprocal isomerides* may be applied to this class of bodies. Ethyl formate and methyl acetate, propyl formate and methyl propionate furnish examples.

A third class to which the authors apply the name *isomerides by compensation*, includes not only compound ethers which belong at the same time to the class of reciprocal isomerides (as, for instance, butyl acetate and ethyl butyrate), but more generally all in which the deficiency of carbon and hydrogen in one of the constituent radicles is made up by a corresponding increase in the other. Ethyl valerate and propyl butyrate furnish an example.

In a considerable number of the pairs of isomerides belonging to the last two classes, the authors have traced an almost complete identity of properties, extending to boiling point, odour, specific gravity at 0° and at boiling point, and specific volume. In a few cases, there is a difference of some degrees in the boiling point, and slight discordance between the numbers representing the density and specific volume of the liquids under comparison. Whether the values thus obtained are to be regarded as merely approximate, and likely on re-examination to be replaced by others exhibiting the perfect agreement so strikingly shown by the others, is a point upon which the authors are undecided.

W. A. T.

[*Note by Abstractor.*—General formulæ for these pairs of isomeric ethers may be written more concisely.

$$\left\{\begin{matrix} CO.C_mH_{2m+1} \\ O.C_nH_{2n+1} \end{matrix}\right., \quad \text{and} \quad \left\{\begin{matrix} CO.C_{m_1}H_{2m_1+1} \\ O\,C_{n_1}H_{2n_1+1} \end{matrix}\right.$$

Where

$$m + n = m_1 + n_1.$$

The constitutional formulæ of those pairs of ethers in which there is identity of properties, show that they contain the same atomic groups and the same number of groups, though of course in different order.

This will be seen in the following examples. The boiling points and other numbers are those given by the authors.

	Ethyl isovalerate. $\begin{cases} CO.CH_2CH(CH_3)_2 \\ O.CH_2CH_3 \end{cases}$	Propyl isobutyrate. $\begin{cases} CO.CH(CH_3)_2 \\ O.CH_2CH_2CH_3 \end{cases}$
Boiling point	135·5°	135°
Density at 0°	·886	·887
,, at b.p.	·744	·745
At. vol. at b.p.	2184	2181

In those cases, however, in which the authors find only a close resemblance but not identity in properties, an examination of the constitutional formulæ will show that the two substances, though possessing the same total composition, do not contain exactly the same atomic groups.

The following are two examples taken from the paper:—

	Propyl formate. $\begin{cases} CO.H \\ O.CH_2CH_2CH_3. \end{cases}$	Ethyl acetate. $\begin{cases} CO.CH_3 \\ O.CH_2CH_3. \end{cases}$
Boiling point	82·7°	73°
Density at 0°	·919	·907
,, at b.p.	·823	·814
At. vol. at b.p.	1337	1349

	Isobutyl acetate. $\begin{cases} CO.CH_3 \\ OCH_2CH(CH_3)_2. \end{cases}$	Propyl propionate. $\begin{cases} CO.CH_2CH_3 \\ O.CH_2CH_2CH_3. \end{cases}$
Boiling point........	116·5°	124·75°
Density at 0°	·905	·902
,, at b.p.......	·778	·763
At. vol. at b.p.......	1864	1900

The authors appear to take no account of the differences which might be expected to occur in comparing derivatives of the normal and iso-alcohols.

W. A. T.

Combined Action of Heat and Pressure upon the Paraffins. By T. E. Thorpe and J. Young (Ann. Chem. Pharm., clxv, 1—28).

A short abstract of this paper has already been published in this Journal ([2] x, 802). The present communication gives a full description of the experiments, modes of separation, and analyses of the different products.

C. S.

Nitro-Compounds of the Fatty Series. III. By V. Meyer and A. Rilliet (Deut. Chem. Ges. Ber., v, 1029—1034).

The compound obtained by precipitating nitromethane with alcoholic potash has the composition $CH_2Na(NO_2) + C_2H_6O$, and loses the ethyl alcohol when it is kept over sulphuric acid. The sodium-compound can be kept in closed vessels without undergoing any change, but on exposure to the air it rapidly decomposes, and a concentrated aqueous solution undergoes, in a few minutes, spontaneous decomposition with elevation of temperature.

The corresponding mercury-compound is obtained as a yellow powder by precipitating the sodium-compound with a solution of mercuric chloride. In the dry state it is a most dangerous substance, which, when stirred up with a glass rod, explodes with fearful violence.

In order to obtain nitroacetone, acetyl chloride was added to the sodium-compound suspended in ether. On adding water after the very violent reaction was over, white flakes separated out, consisting probably of a product of condensation.

By acting with acetic anhydride on nitro-ethane, a crystalline solid, fusing at a low temperature, was obtained, which appears to be *nitro-ethyl-methyl ketone*, $C_2H_4NO_2$—CO—CH_3.

When sodium-nitromethane is acted upon by chlorocarbonic ether in presence of absolute alcohol or ether, a brown oily body is formed, which is carbonized by distillation; it is not improbable that this substance is nitroacetic ether.

By adding bromine to an aqueous solution of sodium-nitro-ethane, a heavy oil is obtained, which, when freed from some unaltered nitro-ethane, boils at 152°—157°, and smells like chloropicrin. This compound contains 10 per cent. more bromine than that required by the formula $C_2H_4Br(NO_2)$. It dissolves with rise of temperature in concentrated caustic potash, and on cooling, crystals resembling potassium picrate separate out. It is very explosive, not only in the dry state, but also in concentrated solution. On touching a thick glass tube containing the liquid with a red-hot glass rod, it was shattered to pieces. This body is, perhaps, the potassium compound of nitro-ethyl alcohol $C_2H_4(NO_2)OK$.

Normal nitropropane, $C_3H_7NO_2$, is produced, together with some propyl nitrite, by the action of propyl iodide on a mixture of equal volumes of dry silver nitrite and sand. It is a limpid mobile liquid, very little heavier than water, and boiling at 122°—127°. Its properties are very similar to those of nitroethane. The sodium-compound gives characteristic precipitates with salts of the heavy metals. (See next paper.)

C. S.

Nitro-Compounds of the Fatty Series. IV. By V. Meyer and C. Chojnacki (Deut. Chem. Ges. Ber., v, 1034—1038).

In the preparation of nitroethane part of the ethyl iodide always remains unacted upon, whilst other iodides are completely decomposed by silver nitrite. To convert all the ethyl iodide into the nitro-compound, the

product of the reaction is first distilled from a water-bath as long as ethyl iodide mixed with some nitroethane comes over, and then the pure nitroethane left behind is distilled from an oil-bath. The residue is powdered, and the first distillate gradually added to it, when all the iodide will be converted into the nitro-compound.

Isonitropropane is obtained, together with isopropyl nitrite, in a similar way as the other nitro-compounds. It boils at 112°—117°, its sodium-compound is deliquescent, and more soluble than that of normal nitropropane.

The heavy metals give, with the sodium-compounds of nitro-methane, nitroethane, and the two nitropropanes, such characteristic precipitates, that these reactions may be used for distinguishing these nitro-compounds, as the following table shows. Nitropentane does not form metallic compounds.

	Mercuric chloride.	Mercurous nitrate.	Ferric chloride.
Sodium nitromethane	Light yellow precipitate; explosive.	Black flocculent precipitate.	Dark brownish-red precipitate.
Sodium nitroethane	White crystalline precipitate.	Dirty-grey precipitate.	Blood-red coloration.
Sodium nitropropane (normal)	White crystalline precipitate.	Black flocculent precipitate.	Blood-red solution.
Sodium nitropropane (iso)	White crystalline precipitate.	Black flocculent precipitate.	Blood-red solution.

	Barium chloride.	Copper sulphate.	Lead acetate.	Silver nitrate.
Sodium nitromethane	0	Grass green precipitate.	White precipitate.	White precipitate, turning almost immediately black.
Sodium nitroethane	0	Deep green solution.	0	White precipitate, soon turning brown.
Sodium nitropropane (normal)	0	Deep green solution.	White precipitate.	White precipitate gradually turning brown.
Sodium nitropropane (iso)	0	Deep green solution.	0	Light-yellow precipitate, soon turning black.

C. S.

Perchlorinated Methylmercaptan. By B. RATHKE (Deut. Chem. Ges. Ber., v, 798).

THIS body is easily obtained by acting upon carbon sulphide containing a little iodine with dry chlorine, with the aid of heat. Besides the

CCl_4 and SCl_2 formed at the same time, there is at least one other product, a body which crystallises out after the distillation of the more volatile products, and when recrystallised forms shining prisms having the composition $C_2Cl_6S_3$. This body is resolved by distillation into $CSCl_3$ and SCl_2. The compound $CSCl_3$ is more easily obtained by treating CCl_4S with finely-divided silver.

J. R.

Action of Carbon Sulphochloride and Perchlorinated Methylmercaptan on Aniline. By B. Rathke (Deut. Chem. Ges. Ber., v, 799).

$CSCl_2$, acting on aniline not in excess, forms phenyl sulphocyanate; with excess of aniline the product is diphenylurea, which is converted by more $CSCl_2$ into phenyl sulphocyanate. $CSCl_4$ in ethereal solution, yields with aniline not in excess, the compound $CCl_3S.C_6H_5$ a thick oil, which decomposes in the water-bath, evolving hydrochloric acid; it is converted by alcoholic potash into $CHCl_2S(O.C_6H_5)$, a body crystallising in long prisms. $CSCl_4$, with excess of aniline (more than 2 mol.), acts in the same way at first, but after evaporating the ether, the residue solidifies, triphenylguanidine being formed.

J. R.

Behaviour of Ether in Contact with various Substances. By A. Lieben (Ann. Chem. Pharm., clxv, 134).

Pure ether, when shaken with water, does not communicate to the water anything capable of yielding the iodoform reaction when treated with iodine and potash; such ether can be obtained by distilling purified ether two or three times over sodium, the entrance of moisture being prevented by means of a chloride of calcium tube; such ether does not give the iodoform reaction even after standing 1½ year in well-closed vessels; if, however, it be mixed with water or dilute sulphuric acid, and heated to 100° for a day, a strong iodoform reaction is obtained, and when it is kept in contact with water at the ordinary temperature for three or four months, the same result ensues.

Pure ether sealed up with fragments of sodium, caustic potash, or potassium carbonate, was unaffected even after many months; but in contact with calcium chloride, sodium chloride, or copper sulphate (anhydrous) decomposition took place, and a body which yielded the iodoform reaction was produced.

The author concludes that bases do not cause this change in ethers, while neutral salts and acids do; possibly ethylates are formed, thus—

$$CuSO_4 + C_2H_5O.C_2H_5 = Cu\left\{\begin{matrix} OC_2H_5 \\ O.SO_2.OC_2H_5, \end{matrix}\right.$$

or possibly the ether splits into alcohol and ethylene.

C. R. A. W.

Ethyloxy-oxalyl Chloride. By L. Henry (Deut. Chem. Ges. Ber., v, 919).

In the hope of obtaining either the ether of a ketonic acid (C_nH_{2n+1})—CO—$CO(OC_2H_5)$, or that of a tertiary alcohol acid $C(C_nH_{2n+1})_2(OH)$ $-CO(OC_2H_5)$, the action of organo-zinc radicals on ethyloxy-oxalyl-chloride, $COCl$—$CO(OC_2H_5)$ was examined.

Two proportions of zinc-ethyl and one of this latter substance were gradually mixed in a cooled vessel; a vigorous reaction ensued, and a combustible colourless gas, probably ethane, C_2H_6, was evolved: on addition of water, more ethane escaped, and zinc hydrate was formed, an oily layer being separated; the whole was distilled and the distillate treated with potassium carbonate; the oily fluid produced boiled at 175°—176° at 750 mm., and had the vapour-density 5·36; it was found to be identical with the ethyl-diethylglycollate, or ethyl-leucate, of Frankland and Duppa, $C(C_2H_5)_2(OH)$—$CO(O.C_2H_5)$.

Hence, when ethyloxy-oxalyl chloride is subjected to treatment with zinc-ethyl and water, the product bears to it the relation of a tertiary alcohol to an ordinary oxychloride $(C_nH_{2n+1})COCl$; when ketones bodies of this latter kind are similarly treated, however, are formed and not tertiary alcohols (Butlerow).

In the hope of obtaining mesoxalic ether by the decomposition of potassium ethyloxalate thus—

$$\begin{array}{l} CO(OC_2H_5) \\ | \\ CO(OK) \\ CO(OK) \\ | \\ CO(OC_2H_5) \end{array} = CO\begin{Bmatrix} OK \\ OK \end{Bmatrix} + \begin{array}{l} CO(O.C_2H_5) \\ | \\ CO \\ | \\ CO(O.C_2H_5) \end{array}$$

this latter was carefully heated with about twice its weight of sand. Alcohol and oxalic ether were obtained as a distillate; possibly, therefore, the potassium ethyloxalate becomes potassium oxalate + ethyl oxalate on heating; or possibly the nascent mesoxalic ether is further decomposed into oxalic ether and CO.

The author proposes to obtain the aldehyde corresponding to ethyloxy-oxalyl chloride, viz., COH—$CO(OC_2H_5)$, and also that corresponding to the ethyl-oxyglycollyl chloride, $COCl - CH_2(O.C_2H_5)$, previously described by him, viz., $COH - CH_2(O.C_2H_5)$: these bodies would be the ethers of glyoxylic and glycollic aldehydes respectively:—

$$COH—CO(OH), \text{ and } COH—CH_2(OH).$$

C. R. A. W.

Decomposition of Chloral Hydrate by the Combined Action of Glycerin and Heat. By H. Byasson (Compt. rend., lxxv, 1628—1630).

When chloral hydrate is heated with five times it weight of syrupy glycerin, a regular reaction begins at 110° and goes on up to 230°, at

which temperature the operation has to be stopped, in order not to complicate the results. The distillate consists of chloroform, formic acid and undecomposed chloral hydrate, besides some hydrochloric acid and allyl formate, which are secondary products.

C. S.

Use of the Compound of Dextroglucose and Sodium Chloride for the Titration of Fehling's Solution. By C. Scheibler (Deut. Chem. Ges. Ber., v, 802).

The compound $2C_6H_{12}O_6.NaCl + H_2O$, is easily obtained in beautiful crystals, by allowing a concentrated solution of grape-sugar (as free as possible from dextrin) and sodium chloride to stand for some time. The crystals, which are permanent in the air, neither hygroscopic nor efflorescent, are recommended by the author for the titration of Fehling's solution.

J. R.

Preparation of Pure Dextroglucose. By Professor Schwarz (Deut. Chem. Ges. Ber., v, 802).

Cane-sugar is added to 80 p.c. alcohol containing a little hydrochloric acid. The sugar gradually dissolves, and after a time chemically pure dextroglucose is deposited.

J. R.

Derivatives of Sulphocarbamic Acid. By H. Hlasiwetz (Deut. Chem. Ges. Ber., v, 802).

Ammonia and carbon bisulphide acting upon each other in presence of a third body (camphor, phenol, &c.), which, according to the author, can exert only a catalytic action, produce large nearly colourless crystals of a compound represented by the formula, $C_2H_{10}N_4S_3$:

$$2CS_2 + 4NH_3 = C_2H_{10}N_4S_3 + H_2S.$$

This compound produces in saline solutions, white precipitates which rapidly blacken: copper-salts alone give a permanent yellow precipitate having the formula $C_2H_3N_2S_3Cu$, showing that the original compound is an ammonium-salt, $C_2H_2N_2S_3(NH_4)_2$. Treated with weak oxidising agents, it yields ammonium chloride and sulphocyanate, and a body $C_2H_4N_2S_4$, which crystallises in shining scales, is nearly insoluble in cold water, and is resolved by boiling with water into ammonium sulphocyanate, carbon sulphide, and sulphur. When aniline is mixed with carbon sulphide and ammonia, an aniline-salt corresponding to the first compound is produced, $C_{14}H_{18}N_4S_3 = C_2H_2N_2S_3(H.C_6H_7N)_2$. It is resolved by boiling with water into sulphocarbanilide, carbon sulphide, and ammonia.

All these bodies are regarded by the author as derivatives of sulphocarbamic acid. The corresponding hydrogen-compound ($C_2H_4N_2S_3$), which has not yet been isolated, stands in the same relation to carbamic acid as does ethyl sulphide to mercaptan.

J. R.

Carbonic and Sulphocarbonic Ethers of Isobutylalcohol.
By E. Mylius (Deut. Chem. Ges. Ber., v, 972—977).

Isobutyl chlorocarbonate, $\left.\begin{matrix}C_4H_9O\\Cl\end{matrix}\right\}CO$, is formed by saturating isobutyl-alcohol with carbon oxychloride. It is a liquid, resembling the ethyl compound, and distilling with much decomposition at 130°—140°. With ammonia it yields *isobutyl urethane,* $\left.\begin{matrix}C_4H_9O\\NH_2\end{matrix}\right\}CO_2$, a solid melting at 55° and boiling at 206°—207°, and not at 220°, as stated by Humann, who obtained it by the action of cyanogen chloride on isobutyl alcohol.

Isobutyl phenylurethane, $\left.\begin{matrix}C_4H_9O\\C_6H_5NH\end{matrix}\right\}CO$, obtained by mixing ethereal solutions of the chlorocarbonate and aniline, crystallises in soft white needles, melting at 80° and boiling at 216°, a small portion being resolved into the alcohol and phenyl cyanate. It is readily soluble in ether and alcohol, but sparingly in water. The corresponding toluidine derivative was obtained from liquid toluidine boiling at 198°. It is an oily liquid, boiling with partial decomposition, at 275°—280°.

Hot isobutyl alcohol forms a syrupy solution with caustic potash. When to the cold liquid carbon sulphide is added, *potassium butyl-xanthonate,* $\left.\begin{matrix}C_4H_9O\\KS\end{matrix}\right\}CS$, separates out. This salt crystallises from alcohol in yellowish white needles, and is resolved by destructive distillation into carbonic oxide, isobutyl sulphide and potassium sulphide. The sodium salt is a similar body, which is very freely soluble in water, alcohol, and a mixture of ether and alcohol.

Isobutyl-ethyl xanthonate, $\left.\begin{matrix}C_4H_9O\\C_2H_5S\end{matrix}\right\}CS$, is obtained by heating the potassium salt with ethyl iodide to 100°. It is a yellow liquid boiling at 227°—228°, having a disagreeable smell and a taste like aniseed. By the action of isobutyl iodide on the potassium salt, the ether $\left.\begin{matrix}C_4H_9O\\C_4H_9S\end{matrix}\right\}CS$ is produced, a liquid boiling at 247°—250°. The corresponding amyl-ether is formed only at 140°. It boils at 265° - 270°, with decomposition, being partly resolved into carbonic oxide, and the sulphides of amyl and isobutyl.

Isobutyl dioxysulphocarbonate, $\left.\begin{matrix}C_4H_9OCS\\C_4H_9OCS\end{matrix}\right\}S_2$, is obtained as a yellow heavy oil when chlorine is passed into an aqueous solution of the potassium-salt. By the action of sodium, it is converted into sodium isobutyl xanthonate, and when ammonia is passed into its ethereal solution, it yields the *semi-sulphuretted urethane,* $\left.\begin{matrix}C_4H_9O\\NH_2\end{matrix}\right\}CS$, crystallising from alcohol or ether in large, yellowish white rhombic plates, melting at 36°. On distillation, the greater portion is resolved into cyanic acid and isobutyl mercaptan.

When ethereal solutions of equivalent quantities of aniline and isobutyl dioxysulphocarbonate are mixed, the liquid becomes warm, sulphur separates out, and on evaporation a residue consisting of a

mixture of isobutyl phenylsulphocarbamate and diphenylsulpho-urea is left behind. In this reaction first the urethane $\left.\begin{matrix}C_4H_9O\\C_6H_5NH\end{matrix}\right\}CS$, is formed, together with aniline isobutyl-xanthonate; the latter compound easily splits up into aniline, carbon sulphide and isobutyl alcohol, and the aniline thus set free transforms the urethane into the sulpho-urea.

To prevent the action of aniline on the urethane, the liquid has to be kept cold, and as soon as the separation of sulphur ceases, a quantity of hydrochloric acid must be added, which is sufficient to neutralise half the aniline employed. The phenyl urethane thus produced, melts at 75°, and has a bitter taste and agreeable odour. It cannot be distilled without decomposition, but evaporates completely on a water-bath.

C. S.

Isobutylsulphonic Acid. By E. MYLIUS (Deut. Chem. Ges. Ber., v, 978).

THIS acid is obtained by oxidising isobutyl mercaptan with nitric acid of spec. grav. 1·30: at the same time an oily compound is formed, which, however, is not the chief product of the reaction, as Humann states, the quantity of it being smaller the purer the mercaptan is, that is to say, the less isobutylsulphide it contains.

By decomposing the lead salt of isobutylsulphonic acid with hydrogen sulphide, and evaporating the solution on a water-bath, isobutylsulphonic acid, $C_4O_9SO_3H$, is obtained as a syrupy liquid, which *in vacuo* over sulphuric acid changes into a crystalline magma. The salts of this acid are all extremely soluble in water. *Silver isobutylsulphonate*, $C_4H_9SO_3Aq$, forms crystalline scales which are not acted upon by light. *Barium isobutylsulphonate* $(C_4H_9SO_3)_2Ba$ is precipitated from a concentrated aqueous solution by alcohol in thin white needles. The *copper salt* forms soft sea-green scales.

C. S.

Caproic Acid, Normal and Ordinary. By A. LIEBEN and A. ROSSI (Ann. Chem. Pharm., clxv, 118).

THE normal acid prepared from normal amyl cyanide was carefully compared with that similarly formed from ordinary amyl cyanide as to the following derivatives:—

Calcium Salt.—The normal acid, supersaturated with milk of lime and after filtration treated with oxalic acid till feebly acid, deposited, on standing *in vacuo*, long prismatic crystals having the composition $Ca(C_6H_{11}O_2)_2.H_2O$, the water of crystallisation being lost at 100°.

The ordinary acid similarly treated yielded crystals containing $Ca(C_6H_{11}O_2)_2.3HO$.

It is noticeable that the calcium salts of all normal acids crystallise with 1 molecule of water. Barone has examined the calcium salt of fermentation butyric acid and finds it to be $Ca(C_4H_7O_2)_2.H_2O$, the composition being the same whether the salt be crystallised out from a

cold liquid or separated from a cold saturated solution by warming; Wrightson similarly finds calcium propionate to be $Ca(C_3H_5O_2)_2.H_2O$; in all these cases the water of crystallisation is lost at 100°. On the other hand, Barone finds that fermentation valerianic acid (from oxidation of the alcohol),—gives the calcium salt $Ca(C_5H_9O_2)_2.3H_2O$, and Markownikoff has shown that calcium isobutyrate contains $Ca(C_4H_7O_2)_2.5H_2O$.

Barium Salt.—The normal salt crystallises on cooling from a hot saturated solution in crystals, which are probably anhydrous.

The ordinary salt is $Ba(C_6H_{11}O_2)_2.2H_2O$, and is less soluble in hot water than in cold.

The solubilities of the above salts are as follows:—

	Calcium salts.		Barium salts.	
	Normal.	Ordinary.	Normal.	Ordinary.
100 parts of solution saturated at 18·5 contain of anhydrous salt	2·7	11·3	8·5	34·65

Ethyl Salts.—These were prepared by mixing the acids with their own weight of nearly absolute alcohol and half as much sulphuric acid, leaving the mixture to stand for several hours, and distilling the upper layer after washing with alkaline solution and with pure water.

	Normal ethyl caproate.	Ordinary ethyl caproate.
Corrected boiling point....	166·5° to 166° at 735 8 mm.	160·4° at 737 mm.
Specific gravity at 0°	0·8898	0·887
" " 20°	0·8732	0·8705
" " 40°	0·8594	0·8566

It is to be noticed that the ordinary caproic acid employed in the above comparison had a very weak optical action; the caproic acid obtained by Franchimont and Zincke from Heracleum oil corresponds exactly with the normal acid, except that its barium salt contains one molecule of water of crystallisation; this the authors consider is not a sufficient difference to warrant the conclusion that the Heracleum acid is only isomeric with normal caproic acid. C. R. A. W.

Didenlactamic Acid and Nitrosodidenlactamic Acid.

By W. Heintz (Ann. Chem. Pharm., clxv, 44—62).

The name *didenlactamic acid* is employed by the author as a convenient abbreviation of the term diethylidenelactamic acid. He also proposes to use the name *didenlactamic acid* in the place of diethylenelactamic acid.

Didenlactamic acid was obtained in an attempt to prepare alanine by Strecker's method (*Ann. Chem. Pharm.*, clx, 35; *Chem. Soc. J.*, 1872, 77).

In this instance the product contained a large quantity of didenlactamic acid and but a small quantity of alanine. It was supposed that the formation of didenlactamic acid took place in consequence of hydrochloric acid being added to the aldehyde-ammonia before the addition of the hydrocyanic acid, but all subsequent attempts to prepare it were fruitless. Notwithstanding this, further investigations of the salts and derivatives of didenlactamic acid have been made.

Acid ammonium salt, $C_6H_{10}(NH_4)NO_4$: obtained by adding excess of ammonia to didenlactamic acid and evaporating to a syrup on the water-bath; on cooling, needles separated which were crystallised from alcohol. The salt separates from this solvent in rectangular tables, but when it is deposited from a mixture of alcohol and ether, it often takes the form of needles. It is very soluble in water, slightly soluble in alcohol, and insoluble in ether. This salt is decomposed at a temperature below its melting point, and on distillation yields ammonia and a thick fluid partly soluble in water. The *barium salt* is obtained by neutralising didenlactamic acid with excess of barium hydrate, removing the superfluous base by means of carbonic anhydride and evaporating the slightly alkaline liquid. The syrupy residue which remains gradually dries up to a brittle fissured mass. If alcohol be added to an aqueous solution of this salt the latter is separated in a syrupy form. The action of acetic acid on it did not give rise to the formation of a crystalline acid salt. *Zinc salt*, $C_6H_9ZnNO_4$: obtained by boiling didenlactamic acid with basic zinc carbonate and a considerable quantity of water, filtering hot, and evaporating. It consists of microscopical quadratic tables, very slightly soluble in water, but easily soluble in hydrochloric acid. *Cadmium salt*, $C_6H_9CdNO_4$: obtained by boiling a dilute aqueous solution of didenlactamic acid with cadmium carbonate, evaporating the solution, treating the residue several times with hot water, and pressing the undissolved portion. It may be obtained in microscopic needles by boiling its cold saturated solution. This salt is very soluble in cold water, although it dissolves but slowly. The solution, on evaporation over sulphuric acid, yields a syrupy residue, which gradually becomes opaque and partially solid. While the syrup remains transparent it dissolves readily in cold water, but when it has become solid and opaque it is no longer easily soluble. The author considers that the change into the less soluble variety is accompanied by partial dehydration. On boiling a cold saturated solution, the partially dehydrated salt is deposited in needles having the composition $C_6H_9CdNO_4 + H_2O$. The salt dried at 150° contains $C_6H_9CdNO_4$. *Lead salt*, $C_6H_9PbNO_4$, an aqueous solution of didenlactamic acid saturated with lead hydrate forms a strongly alkaline liquid, from which almost all the excess of lead may be removed by means of carbonic anhydride. By filtering this solution, slightly acidulating with acetic acid, evaporating and adding alcohol, crystalline crusts of a lead salt were obtained; when crystallised from dilute alcohol it has a slightly alkaline reaction. The *silver salt*, $C_6H_9Ag_2NO_4$, is obtained as a white precipitate when a soluble salt of didenlactamic acid is precipitated by silver nitrate. Like silver diglycollamate, it explodes slightly when heated. From boiling water it separates partly in small rhombic tables, partly in needles, which are sometimes united in tufts.

Hydrochloride of Didenlactamic Acid.—When didenlactamic is dissolved in fuming hydrochloric acid and the solution is evaporated *in vacuo*, a syrup-like mass is obtained which dissolves in a small quantity of absolute alcohol, and is separated from it in the fluid state on addition of water. If the previously mentioned solution be evaporated, and the residue be dissolved in a small quantity of water, it yields on evaporation over sulphuric acid, a syrup-like mass, in which flat microscopic needles gradually form. If, however, the residue be dissolved in absolute alcohol and ether be added, small crystals are deposited, which consist of a compound soluble in alcohol or ether and permanent in the air. This substance dissolves in water, and the solution on spontaneous evaporation yields colourless crystals, consisting of rhombic prisms. Analysis showed it to be a compound of two molecules of didenlactamic acid and one of hydrochloric acid.

Nitrate of Didenlactamic Acid.—Didenlactamic acid dissolves readily in nitric acid, and the solution, when evaporated over sodium hydrate, gives a thick syrup, which, when dissolved in warm alcohol and separated by the cautious addition of ether, takes the form of fringed hemispherical grains, which appear to consist of groups of fine concentric needles. This compound was not analysed.

Nitroso-didenlactamic Acid.—Calcium nitrite was added, in small portions at a time, to a solution of didenlactamic acid in nitric acid, the solution being kept in motion to prevent local heating. Sufficient calcium nitrite having been added to make the liquid permanently green, it was diluted, gently warmed, neutralised with lime, and evaporated almost to dryness. By dissolving the residue in alcohol and adding ether, a precipitate consisting of the calcium salt of the new acid was obtained. The free acid may be obtained from this salt either by decomposing it with the requisite quantity of oxalic acid, or by precipitating it with ammonia and ammonium carbonate, boiling the ammonium salt thus obtained with barium hydrate, and decomposing the barium salt with the requisite quantity of sulphuric acid.

The free acid forms a syrup which finally solidifies to small colourless flat needles, consisting partly of elongated rhombic tables and partly of elongated six-sided tables. It is easily soluble in water or alcohol, and is dissolved by ether. With concentrated sulphuric acid and ferrous sulphate it gives the well-known reaction characteristic of the higher oxides of nitrogen. Analysis of its calcium salt led to the formula, $C_6H_8(NO)CaNO_4$.

The author considers that the properties of the compounds just described, and more especially the formation of nitrosodidenlactamic acid, prove satisfactorily the analogy between didenlactamic acid and diglycollamic acid.

T. B.

Reciprocal Transformation of Inactive Tartaric Acid and Racemic Acid. Preparation of Inactive Tartaric Acid.

By E. JUNGFLEISCH (Compt. rend., lxxv, 1769—1773).

DURING the reaction described in the author's former paper (p. 166 of this volume), a certain quantity of inactive tartaric acid is always formed

along with the racemic acid. This, when the question is fully investigated, becomes a matter of great consequence. It is important to decide, in studying the reaction, whether a complete transformation of the dextrotartaric acid, at a single operation, is possible, or whether, the temperature being kept at 175°, a state of equilibrium supervenes between the transformed and the non-transformed acid. The former was found to be the case. The whole of the dextrotartaric acid is transformed under a prolonged application of the high temperature. What, then, is the reason why the whole of it cannot be turned into racemic acid except by the successive operation described above? It is found that this is due to the formation of inactive tartaric acid, and that between these two bodies in solution and the water a state of equilibrium is arrived at after long heating. The mother-liquor spoken of above, contains, if the operation has been pushed till all the dextrotartaric acid has disappeared, only inactive tartaric acid, which is very soluble, and the small proportion of the racemic acid which has not crystallised. On concentrating and re-heating, a new proportion of racemic acid is formed, and an equivalent of the inactive acid disappears. Again, when pure inactive tartaric acid is heated in a closed tube to 175°, a precisely similar reaction occurs, racemic acid is formed, and the whole of the inactive tartaric acid may be converted into racemic acid. The reaction reciprocal to this leads to a method of preparing inactive tartaric acid. When pure racemic acid is heated, a portion of it is converted into the inactive acid. This being very soluble, can be removed in the liquor which remains after crystallising out the unconverted racemic acid. On adding a small quantity of water to the crystals, and heating again, a further quantity of inactive acid is obtained, and the process may be carried on till almost the whole of the racemic acid is transformed. In fact, all that is left is the small quantity that is carried away uncrystallised by the liquors obtained in the successive operations. This small quantity is afterwards removed by concentrating them and crystallising again.

In practice, however, it is found that at a lower temperature than 175°, a larger proportionate quantity of inactive acid is formed. The best result appears to be obtained at 165°. If dextrotartaric acid be treated on the plan described for the preparation of racemic acid, the temperature being kept at 165°, only a small quantity of racemic acid is formed at each operation, and the whole may, by successive operations, be transformed into the inactive acid. In this way, the author has obtained as large a quantity as $1\frac{1}{2}$ kilograms ($3\frac{1}{3}$ lbs.) of inactive tartrate of potassium with a very small apparatus.

This process is important; for the inactive acid, discovered by Pasteur, has hitherto been a very rare substance. The author of the present paper has compared his acid with inactive tartaric acid furnished by Pasteur, and finds the two in every respect identical.

Theoretically considered, the experiment described has great interest. It appears that the relative quantities of the two acids and of the water necessary to give a state of equilibrium, depend on the temperature at which the experiment is performed: that is to say, at lower temperatures a larger quantity of inactive tartaric acid, and at higher temperatures a larger quantity of racemic acid is required for the

equilibrium state. This also furnishes a new example of the phenomenon observed by Berthelot and Péan de Sainte-Gilles, first with regard to the ethers, and subsequently with regard to other bodies present in the same solution.

J. T. B.

Action of Benzyl Chloride on Aromatic Hydrocarbons. By TH. ZINCKE (Deut. Chem. Ges. Ber., v, 799).

THE author, by acting upon isoxylene and paraxylene with benzyl chloride, in presence of zinc, has obtained benzylisoxylene and benzylparaxylene, both having the formula $C_{15}H_{16}$, or $C_6H_5.CH_2.C_6H_3(CH_3)_2$. Benzylisoxylene is a colourless liquid, of feeble aromatic odour, boiling at 295°—296°. Benzylparaxylene is a similar liquid, boiling at 293·5°—294·5°. The former body, when oxidised with potassium chromate and sulphuric acid, yields benzylisophthalic acid, $C_6H_5.CO.C_6H_3(CO_2H)_2$, which is sparingly soluble in benzene and chloroform, easily soluble in alcohol, ether, and glacial acetic acid, and melts at 278°—280°. This acid forms barium- and calcium-salts much more soluble in cold water than in hot. By reduction with zinc and hydrochloric acid, it yields an acid, $C_{15}H_{10}O_4$, which crystallises in long shining prisms, melting at 206°, and decomposible by hydriodic acid.

J. R.

Nitrotoluene. By A. ROSENSTIEHL (Ann. Chim. Phys. [4], xxvii, 433—476).

AFTER describing a series of experiments confirming the observation that liquid (α) nitrotoluene yields on reduction, the liquid modification of toluidine (pseudo-toluidine), the author proceeds to detail a long series of fractional distillations which he carried out in order to ascertain if it be possible to obtain the liquid modification of nitrotoluene in a pure state by this method. The purest product which he obtained by distillation yielded a mixture of toluidines containing 13·7 per cent. of the crystallisable variety, and an attempt to obtain the liquid nitrotoluene in a pure state by fractional condensation led to a similar result. These results are at variance with those of Beilstein and Kuhlberg, who state that crude nitrotoluene, when fractionated, splits up into solid nitrotoluene boiling at 235°—236°, and liquid nitrotoluene boiling at 222°—223°.

As solid nitrotoluene yields nitrodracylic acid when it is treated with chromic acid, and, according to the author's latest results, liquid nitrotoluene does not yield nitrodracylic acid by oxidation, it was considered probable that pure liquid nitrotoluene might be obtained by treating the mixture with chromic acid. It was found, however, that by treating a mixture containing 13·7 per cent. of solid nitrotoluene with chromic acid until scarcely any further action took place, a product was obtained which, on reduction, yielded mixed bases containing 8·75 per cent. of solid toluidine. Oxidation with potassium permanganate led to a similar result.

In order to determine whether the two modifications of nitrotoluene

are derived from two isomeric toluenes, or from the same hydrocarbon, the author endeavoured to convert the toluidines into the corresponding toluic acids by the method pointed out by Hofmann, hoping to obtain the hydrocarbons by distillation of these with baryta; but as the products were exceedingly small in quantity, this branch of the investigation was discontinued. Afterwards Berthelot studied the action of hydriodic acid on a sample of pure liquid toluidine furnished to him by the author, and found that this substance, when heated to 270° with 60 parts of hydriodic acid, yielded heptylene and ammonia; but when it was heated with 40 parts of hydriodic acid, toluene was formed, together with traces of benzene and some more condensed hydrocarbons. The toluene thus produced appeared to be identical with that produced by the action of hydriodic acid on crystallised toluidine, each yielding, when nitrated and reduced, a mixture of solid toluidine and liquid toluidine. Berthelot also communicated to the author the fact that both toluene which has been subjected to a red heat and toluene from xylene, yield a mixture of the two toluidines. The author has found that the toluene prepared from tolu balsam also furnishes a mixture of the isomeric alkaloids, and it is evident that the toluidine prepared by Noad, from toluene derived from toluic acid, contained uncrystallisable toluidine, as he refers to it as an oil which crystallised only after purification. Toluidine prepared from synthetically produced toluene contains, according to the author, 46 per cent. of liquid toluidine. Moreover, Berthelot has found that the toluenes which he obtained by the reduction of mono- di- and tribenzylamine yield both toluidines. As all these toluenes yield both solid and liquid toluidine, and consequently both the nitro-compounds, it is natural to conclude that when toluene is nitrated, both nitro-derivatives are always formed. In order further to elucidate this point, portions of the same sample of toluene were nitrated, and it was found that the isomeric nitro-derivatives were produced in proportions varying according to the conditions of the operation, the crystallised nitrotoluene being formed in the larger proportion when the action was most energetic, and the liquid modification predominating when the action was more moderate.

As the proportion of crystallised nitrotoluene in the product never exceeded 64·8 per cent., or fell below 33·3 per cent., it would appear that the amount formed of either isomeride never exceeds two-thirds of the whole product, and that either modification can be formed in the proportion of 2 : 1. These observations, taken in conjunction with the fact, proved by the author, that nitric acid continues its nitrating action on toluene until its strength has become reduced to that corresponding with the formula $(NO_3H)_2.3H_2O$, led to the conclusion that the formation of the nitrotoluenes may be satisfactorily represented by the following equations:—

$$(1.)\ 3(C_7H_6.H\alpha H\beta) + 5NO_3H = C_7H_6(NO_2)\alpha H\beta + 2(C_7H_6H\alpha(NO_2)\beta) + (NO_3H)_2 3H_2O.$$

$$(2.)\ 3(C_7H_6H\alpha H\beta) + 5NO_3H = 2(C_7H_6(NO_2)\alpha H\beta) + C_7H_6H\alpha(NO_2)\beta + (NO_3H)_2 3H_2O.$$

The two limits of the action are represented above. When both reac-

tions take place simultaneously, intermediate proportions are obtained. The author considers it probable that similar limits will be observed in other cases of the formation of isomerides. It is obvious that these limits depend on the number of molecules taking part in the reaction (m), and on the number of hydrogen atoms (n) in each molecule capable of replacement and occupying different positions. The limits within which the proportion of the isomerides can vary, may therefore be represented by the formula $(m - n) + 1 : 1 : 1$, it being understood that m and n are integral numbers, that m is not less than 1, and that n is not less than 2. In order to show that nitrotoluene is not a mixture of three isomerides, the author assumes the formation of a third modification. In this case we have $m = 3$ and $n = 3$, and the above formula indicates the formation of the three isomerides in the ratio of $1 : 1 : 1$, that is to say, they could only be formed in equal quantities. This cannot be true, as each of the two known isomerides was obtained in the proportion of $2 : 1$, and it is impossible that the (supposed) third modification should be confounded at one time with the solid and at another with the liquid nitrotoluene. Therefore nitrotoluene is a mixture of only two isomerides.

A short summary of the properties of the nitrotoluenes is given, in which the descriptions are not always in accordance with those of Beilstein and Kuhlberg.

Alpha-nitrotoluene, the para-nitrotoluene of Beilstein and Kuhlberg; colourless prisms having a slight but persistent odour recalling that of anise. Solidifies at + 52°, and distils without change at 237°—238°. It is almost insoluble in water, but readily soluble in alcohol, ether, and liquid nitrotoluene. It corresponds with crystallised (α) toluidine, and is converted into nitrodracylic acid by treatment with chromic acid. When pure it is converted into alpha-dinitrotoluene by the action of nitric acid, but when mixed with a large proportion of its liquid isomeride it is oxidised by nitric acid.

Alpha-dinitrotoluene; the meta-para-dinitrotoluene of Beilstein and Kuhlberg. Prepared as above. Solidifies at + 70°. Is oxidised with extreme slowness by fuming nitric acid, a small quantity of an acid being formed which has been recognised as dinitrobenzoic acid by Tiemann and Judson.

Beta-nitrotoluene; the meta-nitrotoluene of Beilstein and Kuhlberg. Has not been obtained in a pure state by the author, the purest obtained by him being contaminated with 8·76 per cent. of alpha-nitrotoluene, and boiling between 219° and 220°. It is a clear yellowish liquid having an odour recalling that of nitrobenzene. It corresponds to liquid (pseudo- or meta-) toluidine, and does not yield an isomer of nitrodracylic acid on treatment with chromic acid. When it is oxidised by nitric acid, a small quantity of nitro-dracylic acid is formed; but the author attributes this result to the presence of alpha-nitrotoluene. With fuming nitric acid a crystalline product, apparently identical with alpha-binitrotoluene, is obtained, together with an oily substance, which the author regards as a dinitrotoluene.

In the remaining portion of the paper the author endeavours to prove that Beilstein and Kuhlberg did not obtain beta-nitrotoluene in a state of purity.

T. B.

Iodo-derivatives of the Orcins. (Preliminary Notice.) By J. Stenhouse (Chemical News, xxvi, 279).

Monoiod-orcin, $C_7H_7IO_2$. When an ethereal solution containing a molecule of orcin and one of iodine is agitated with dry precipitated mercuric oxide, the colour rapidly disappears and an iod-orcin is formed. On distilling off the ether and exhausting the residue with hot benzene, the iod-orcin separates in the crystalline state on cooling. In this reaction powdered litharge may be advantageously substituted for the mercuric oxide, since the lead iodide produced is not dissolved when the residue is extracted with benzene. Two or three alternate crystallisations from benzene and from water suffice to render the iodide pure; but, if mercuric oxide has been used, it is advisable to use a dilute solution of potassium iodide for the first crystallisation, to prevent the mercuric iodide crystallising out along with the iod-orcin. Monoiod-orcin, as thus prepared, is a colourless crystalline substance which melts at about 86°, and decomposes, with evolution of iodine vapours, when heated more strongly. Gently heated with concentrated sulphuric acid, the substance is decomposed and iodine freely liberated. Iod-orcin is only slightly soluble in cold water, but readily in hot water. It is very soluble in ether and in hot alcohol; moderately soluble in benzene, and in hot petroleum, crystallising out from the latter almost entirely on cooling; slightly soluble in carbon sulphide. It is quite destitute of the peculiar astringent sweet taste so characteristic of pure orcin.

Monoiodo-resorcin, $C_6H_5IO_2$. This compound, prepared in a similar manner to the corresponding orcin compound, is a colourless crystalline substance, closely resembling the iod-orcin in its general characters, but much more soluble in water.

When the monoiod-orcins in ethereal solution are again treated with iodine and a metallic oxide, more of the hydrogen is replaced, producing the higher iodo-compounds.

J. B.

Accidental formation of Calcium Rosolate. By G. Leuchs (J. pr. Chem. [2], vi, 159).

In the demolition of a tar-covered roof, some portions of mortar directly underlying the tar, in situations which had not been exposed to wet, were found of a deep-red colour. The colouring matter was soluble in water and alcohol, yielding a solution from which hydrochloric acid threw down a precipitate exhibiting all the reactions of Runge's rosolic acid.

J. R.

Monoxyanthraquinone and Anthraflavic Acid. By C. Liebermann (Deut. Chem. Ges. Ber., v, 868—872).

In a former communication the author described monoxyanthraquinone, $C_{14}H_7(O_2)''OH$, a compound which is obtained as a bye-product in the manufacture of artificial alizarin; afterwards he and Graebe showed

that the same compound is produced by fusing monobromoanthraquinone or anthraquinone-monosulphonic acid with potash. Schunck isolated from commercial artificial alizarin a very similar compound, which he calls anthraflavic acid, and to which he assigns the composition $C_{15}H_{10}O_4$, whilst according to Perkin and Auerbach, the formula of this bye-product is $C_{14}H_8O_4$, according to which it is an isomeride of alizarin. The author having lately obtained a fresh sample prepared from the same commercial alizarin from which Auerbach had isolated it, analysed it again, the results being a confirmation of his former analyses.

When oxyanthraquinone is heated with acetic anhydride to 160°, *acetylanthraquinone*, $C_{14}H_7(O_2)''OC_2H_3O$, is produced, crystallising from alcohol in very small, nearly colourless, interwoven needles, melting at 158°. By treating alizarin in the same way it yields diacetylalizarin, $C_7H_6(O_2)''(OC_2H_3O)_2$, which separates from alcohol as a yellow amorphous powder.

C. S.

On Sulphobenzophenone and a Product of the Distillation of Barium Benzoate. By A. Behr (Deut. Chem. Ges. Ber., v, 970—972).

Sulphobenzophenone, $CS\left\{\begin{matrix}C_6H_5\\C_6H_5\end{matrix}\right.$ is readily formed by the action of an alcoholic solution of potassium hydrosulphide on the chloride of benzophenone. It crystallises from carbon sulphide in large prisms, and from hot glacial acetic acid in slender white needles grouped in globular masses, and melting at 152°—153°. Oxidising agents convert it again to benzophenone. When heated above its melting point, it first turns blue and then green, hydrogen sulphide being given off at the same time. On distillation, a small quantity of a badly smelling oil passes over, whilst another portion solidifies in the neck of the retort to a crystalline mass of tetraphenylethene, the great part, however, being completely carbonised.

Kekulé and Franchimont obtained in the preparation of benzophenone from calcium benzoate, as bye-products, a hydrocarbon melting at 145°, and anthraquinone.

The author has found that besides these bodies, some anthracene is formed, and that when barium benzoate is subjected to dry distillation, the hydrocarbon melting at 145° is obtained in larger quantity. This hydrocarbon appears to be *tetraphenylmethane*, and its formation may be explained by the action of benzophenone on benzene in the nascent state:

$$CO(C_6H_5)_2 + 2C_6H_6 = C(C_6H_5)_4 + H_2O.$$

C. S.

Metatoluic Acid. By R. Fittig (Deut. Chem. Ges. Ber., v, 954).

Uvitic acid prepared by Finckh's process from pyrotartaric acid decomposes into metatoluic acid when heated with lime, 1 proportion of the calcium salt and a little more than 1 of lime being the best quan-

tities to employ: at the melting point of lead no action ensues, but at a little higher temperature the decomposition takes place easily. The pure acid melts at 105° (Ahrens found 90°—93°, Tawildarow 85°, Wurtz 90°, Richter 105°—106°, when crystallised from water, 108° when sublimed).

Monobromoxylene, from ordinary xylene of constant boiling point, oxidised by chromic solution yielded the substance described by Ahrens, melting at 92°; on recrystallisation from alcohol, this product gave two different kinds of crystals easily separable mechanically from one another; these were respectively para- and meta-toluic acids.

Finckh considers that the precipitate obtained by adding baryta-water to pyrotartaric acid is a basic salt of that acid; the author finds that when it is treated with carbonic acid, barium carbonate is deposited, and a soluble barium salt, $C_6H_8O_7Ba$, is formed. The acid of this salt is probably—

$$\left.\begin{array}{l} CO(OH)—CH_2(OH)—CH_2 \\ CO(OH)—CH_2(OH)—CH_2 \end{array}\right\} O,$$

whence Wichelhaus' formula for pyrotartaric acid, $\begin{array}{l} CH_2 \\ \,|\quad\rangle O \\ CH \\ \,| \\ CO(OH) \end{array}$, is more probable than the ordinary one, $CH_3—CO—CO(OH)$.

The production of pyrotartaric acid is then explicable, thus—

$$\begin{array}{l} CO.O\,H \\ \,| \\ CH.\,OH \\ \,| \\ CH.O\,H \\ \,| \\ CO.OH \end{array} = \begin{array}{l} CH_2 \\ \,|\quad\rangle O \\ CH \\ \,| \\ CO.OH \end{array} + CO_2 + H_2O.$$

No trimesic acid is produced.

C. R. A. W.

Action of Phosphorus Pentachloride on Sulphonic Acids.

By G. A. BARBAGLIA and A. KEKULÉ (Deut. Chem. Ges. Ber., v, 875—878).

WHEN potassium benzenesulphonate is distilled with an equal weight of phosphorus pentachloride, the chief product consists of benzene sulphochloride, but there is always also some thionyl chloride and monochlorobenzene formed, the quantity of which increases by using more phosphorus pentachloride, and when the sulphochloride is heated with the pentachloride in sealed tubes for some hours to 200°—210°, it is completely decomposed according to the following equation:

$$C_6H_5SO_2Cl + PCl_5 = C_6H_5Cl + SOCl_2 + POCl_3.$$

By distilling potassium phenolparasulphonate with phosphorus

pentachloride, the following products were obtained: *thionyl chloride*, *phosphorus oxychloride*, *dichlorobenzene* melting at 53°—54°, and *monochlorophenylphosphoric acid*, $PO_4(C_6H_4Cl)H_2$, separating from an aqueous solution as a syrup, which soon solidifies to a crystalline mass, melting at 80°, and possessing a phenol-like odour. In this reaction there is also formed, in the first instance, the sulphochloride, $C_6H_4\left\{\begin{matrix}SO_2Cl\\OH\end{matrix}\right.$, which then undergoes a decomposition similar to that of benzene sulpho chloride.

A portion of the monochlorophenol is further acted upon by the phosphorus pentachloride and converted into dichlorobenzene, while another portion by the action of the oxychloride is transformed into monochlorophenylphosphoric acid.

C. S.

Parathionic Acid and Thioamylic Acid, from the Mother-liquors of Coralline. By A. COMAILLE (Compt. rend., lxxv, 1630—1632).

ALFRAISE has shown that the mother-liquors obtained in the manufacture of coralline contain *parathionic acid*, an isomeride of ethyl-sulphuric acid. The author has found that these liquors also contain another acid which, being isomeric with amyl-sulphuric acid, he calls *thioamylic acid*. To obtain these acids, the liquor from which the coralline has been precipitated, is concentrated and heated repeatedly as long as colouring matter is precipitated on addition of cold water. The liquid is then boiled with lead oxide, filtered, and allowed to cool. On standing, red flakes separate out, and the filtrate yields on concentration first the lead salt of parathionic acid, and then that of thioamylic acid. The lead parathionate thus obtained is a basic salt $2(C_4H_{10}O_7S_2).3PbO + 4$ aq.; it crystallises in plates, and is decomposed by the prolonged action of water into an insoluble basic salt containing 4PbO, and the normal salt $C_4H_{10}O_7S_2.PbO.H_2O$, which crystallises in long prisms grouped in stars, or when very slowly evaporated in large, thick hard oblique prisms. The acid forms also a sesquibasic and a monobasic sodium salt. The free parathionic acid is a syrupy liquid, and is neither precipitated by baryta-water nor by lead acetate.

Lead thioamylate, $C_{10}H_{22}O_7S_2.PbO.H_2O$, crystallises in long silky needles, and is very soluble in water, soluble also in absolute alcohol; it has a sweet and bitter taste.

Barium thioamylate, $C_{10}H_{22}O_7S_2.BaO + \frac{1}{2}H_2O$, forms either small masses consisting of very small needles, or oblique prisms. *Potassium thioamylate* is anhydrous, soluble in water and alcohol, and crystallises in oblique pointed prisms. *Ammonium thioamylate*, $C_{10}H_{22}O_7S_2(NH_4)_2O$, is a similar salt. The zinc salt is also very soluble, and forms oblique prisms. *Thioamylic acid* crystallises in long square very deliquescent prisms. When heated, it neither melts nor volatilises, but gives off water before decomposition commences. On boiling its solution for some time, a small quantity of sulphuric acid is formed. Thioamylic acid has great resemblance to amylsulphuric acid; both, as well as their

salts, have a bitter taste, but thioamylic acid is a much more stable compound than its isomeride.

Note by the Abstractor.—There can be scarcely any doubt, that these "new" acids are nothing but phenol-sulphonic and phenol-disulphonic acids; for—

(1.) They are formed by the action of sulphuric acid on phenol in presence of oxalic acid.

(2.) The author has deduced the formulæ simply by determining the metal, sulphur, and water of crystallisation, but has neglected to determine the carbon and hydrogen.

(3.) The molecular weight of phenolsulphonic acid is 174, whilst that of amylsulphuric acid is 168, and phenoldisulphonic acid has the molecular weight 254, being very nearly twice 126, which is the molecular weight of ethylsulphuric acid; from this it follows that the author's analytical numbers are quite in accordance with the composition of phenolsulphonates and disulphonates. Thus he found for his normal lead parathionate:

S = 12·25 and 11·27; PbO = 45·84 and 46·37; H_2O = 4·37 and 4·07.

	S.	PbO.	H_2O.
Calculated for $C_6H_3\left\{\begin{matrix}OH \\ (SO_3)_2Pb\end{matrix}\right. + H_2O$ ..	13·42	46·75	3·77
" " $C_4H_{10}O_7S_2.PbO + H_2O$....	13·47	46·94	3·78

C. S.

Some Substitution-products of Dimethylaniline. By G. KRELL (Deut. Chem. Ges. Ber., v, 878—880).

By the action of chlorine upon pure dimethylaniline, the following compounds are produced:

Monochlorodimethylaniline, $C_6H_4ClN(CH_3)_2$, a very refractive liquid, boiling at about 212°. It forms a highly deliquescent hydrochloride, and a well-crystallised platinum double salt. Its other salts do not crystallise.

Dichlorodimethylaniline, $C_6H_3Cl_2N(CH_3)_2$, is a highly refractive liquid boiling at 234°. None of its salts crystallise with the exception of the platinum compound.

Trichlorodimethylaniline, $C_6H_2Cl_3N(CH_3)_2$, crystallises in needles melting at 32° and boiling at 257°; most of its salts crystallise well.

By the action of nitric acid upon dimethylxylidine, which was produced by Hofmann and Martius' reaction, *dinitrodimethylaniline* $C_6H_3(NO_2)_2N(CH_3)_2$ is obtained in yellowish rhombic plates, melting at 105°. On boiling it with fuming nitric acid, it is converted into *trinitrodimethylaniline*, $C_6H_2(NO_2)_3N(CH_3)_2$, which forms yellow pearly scales, melting at 115°.

C. S.

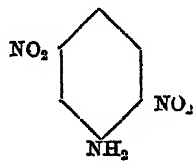
Action of Aqueous Chloride of Lime on an Aqueous Solution of Orthoamidophenol Hydrochloride. By Prof. SCHMITT (Deut. Chem. Ges. Ber., v, 804).

THE latter body (prepared from non-volatile mononitrophenol) is converted by aqueous chloride of lime into dichlorazophenol, $C_{12}H_6Cl_2(OH)_2N_2$. Similarly, aniline is converted into dichlorazobenzene.

J. R.

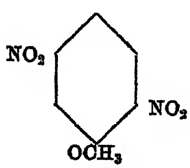
On the Decomposition of the Nitranisols by Ammonia, and the Constitution of Triamidobenzene. By H. SALKOWSKI (Deut. Chem. Ges. Ber., v, 872—875).

WHEN dinitranisol is heated with strong aqueous ammonia in sealed tubes for 3—4 hours to 110°—120°, it is converted into a dinitraniline which is identical with the only known dinitraniline, as both products, when subjected to the action of nitrous acid, yield paradinitrobenzene melting at 87°. The dinitraniline has therefore the following constitution:—

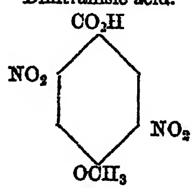


Anisic acid being also a para-compound, their derivatives are constituted as follows:—

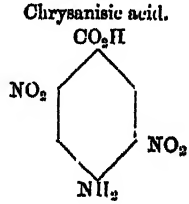
Dinitranisol.



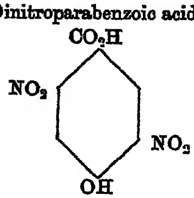
Dinitranisic acid.



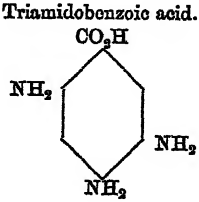
Chrysanisic acid.



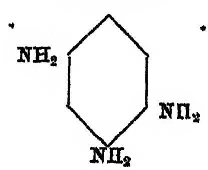
Dinitroparabenzoic acid.



Triamidobenzoic acid.



Triamidobenzene.



Trinitranisol is readily formed by the action of a mixture of nitric and sulphuric acids on dinitranisol; the nitro-groups in this compound are therefore in the position 1, 2, 4, and as trinitranisol is converted

by the action of potash into picric acid, and by ammonia into picramide, it follows that the nitro-groups in picric acid occupy the same positions.

C. S.

Aromatic Amido-acids containing Alcohol-radicles. By P. GRIESS (Deut. Chem. Ges. Ber., v, 1038—1043).

BY the action of ethyl iodide on potassium amidobenzoate, a mixture of ethyl- and diethylamidobenzoic acid is produced, which may be separated by recrystallising the hydrochlorides from hot dilute hydrochloric acid. *Ethylamidobenzoic acid* $C_7H_4(C_2H_5)(HN)O_2$ crystallises in small white or greyish prisms; it is little soluble in hot, and very sparingly in cold water, but dissolves in any proportion in alcohol and ether. The solutions are tasteless, but have an acid reaction. It melts at 112°, and is volatile without decomposition. Like amidobenzoic acid, it has the character of an acid as well as of a base, but does not combine with acetic acid. The hydrochloride forms small four or six-sided plates, and crystallises from hydrochloric acid in needles. It is moderately soluble in cold, freely in hot water, but almost insoluble in cold hydrochloric acid. With platinic chloride it forms a double salt. *Barium ethylamidobenzoate* $[C_7H_4(C_2H_5)(NH)O_2]_2Ba + 2H_2O$ crystallises from water and alcohol in small, indistinct, very soluble plates. Ethylamidobenzoic acid is isomeric with ethyl amidobenzoate, which Cahours obtained by reducing ethyl nitrobenzoate with ammonium sulphide.

When nitrous acid is passed into a moderately concentrated solution of the hydrochloride, or when potassium nitrite is added to it, *nitrosoethylamidobenzoic* acid, $C_7H_4\left(\begin{matrix}C_2H_5\\NO\end{matrix}\right)N.O_2$ separates as a crystalline precipitate. It is sparingly soluble in boiling water, and crystallises therefrom almost completely in yellowish-white long narrow plates. In cold alcohol and ether, it dissolves freely; it is almost tasteless, but has a strong acid reaction and combines with bases but not with acids. The silver-salt forms yellowish-white six-sided small plates, and is but sparingly soluble in boiling water.

Diethylamidobenzoic acid, $C_7H_4(C_2H_5)_2NO_2$, crystallises in perfectly white prisms, having great resemblance to the crystals of ethylamidobenzoic acid. Like the latter, it has no taste, but an acid reaction; it melts at 90°, and can be distilled without decomposition. The hydrochloride, $C_7H_4(C_2H_5)_2NO_2.HCl + H_2O$, is obtained in shining four-sided plates, which are freely soluble in cold water and hydrochloric acid. It loses its water at 130°.

When potassium amidobenzoate is acted upon by allyl iodide, only diallylamidobenzoic acid is produced, crystallising in soft white small plates: it is sparingly soluble in boiling water, but dissolves in any proportion in alcohol and ether, and melts at 90°. The hydrochloride, $C_7H_5(C_3H_5)_2NO_2,HCl + H_2O$, forms large white prisms, which are very sparingly soluble in cold dilute hydrochloric acid; it combines with platinic chloride.

By the action of methyl iodide on amidoanisic acid, *methylamidanisic*

acid, $C_6H_7(CH_3)HNO_3$ is formed, which is isomeric with tyrosine. It forms fine white needles, which are but sparingly soluble in water, and cold alcohol and ether, but freely in hot alcohol. It melts above 200°. The hydrochloride $C_9H_{11}NO_3,HCl + H_2O$, forms very small narrow plates, which are freely soluble in cold water and in hot dilute hydrochloric acid, but only sparingly in cold hydrochloric acid. The silver-salt is a white granular precipitate.

C. S.

The Preparation of Potassium Ferricyanide. By F. RHIEN (Dingl. Polyt. J., ccvi, 151).

To a cold solution of yellow prussiate of potash so much hydrochloric acid is added as will take one atom of potassium from two molecules of the salt, and then a cold clear solution of bleaching-powder till ferric chloride gives no reaction. Any excess of acid is then neutralised with chalk, and the solution evaporated to crystallisation. The first crop of crystals is pure; the subsequent crops contain traces of lime which can be entirely removed by a single recrystallisation. The yield is very large.

C. H. G.

The Behaviour of Certain Metals to a Solution of Potassium Ferricyanide. By R. BÖTTGER (Dingl. Polyt. J., ccvi, 155).

THE author asserts that palladium, thallium, magnesium, and arsenicum possess the power of reducing potassium ferricyanide to ferrocyanide and ferric chloride to ferrous chloride, and states that on laying a strip of pure palladium (not saturated with hydrogen), in a half per cent. solution of potassium ferricyanide for ten minutes, so much of the latter was reduced as to give a distinct reaction with ferric chloride.

C. H. G.

Researches in the Uric Acid Group. (No. III.) By M. NENCKI (Deut. Chem. Ges. Ber., v, 886—889).

CYANOGEN gas passed into a warm aqueous solution of barbituric acid is freely absorbed, and the liquid becomes red. At the same time a crystalline precipitate is deposited, consisting of a new body, *cyanomalonyl-uric acid*. By treating the precipitate with hot water, the red mother-liquor is removed, and the substance so obtained possesses a molecule of water of crystallisation which it loses at 140°. The anhydrous compound has the formula $C_6H_4N_4O_3$, and evidently results from the direct union of cyanogen and barbituric acid:

$$C_4H_4N_2O_3 + C_2N_2 = C_6H_4N_4O_3.$$

Cyanomalonyluric acid dissolved in cold solution of potash furnishes the crystalline potassium salt of a new acid, *cyanuromalic acid*. The potassium salt has the formula $C_6H_5KN_4O_4$. The acid itself is very unstable, and decomposes spontaneously in the air with evolution

of hydrocyanic acid. On boiling it with hydrochloric acid, this decomposition is soon complete, and a crystalline monobasic acid is obtained:

$$C_6H_6N_4O_4 = C_5H_5N_3O_4 + CNH.$$

The acid to which this formula belongs has already been obtained by Baeyer, by heating together barbituric acid and urea:

$$C_4H_4N_2O_3 + CON_2H_4 = \underset{\text{Ammonium malobiurate.}}{C_5H_4N_3O_4.NH_4.}$$

and is regarded by him as malonyl-biuret, $N_3\begin{cases}(CO)_2\\ C_3H_2O_2.\\ H_3\end{cases}$

The acid obtained by the author agrees with Baeyer's malobiuric acid, not only in composition but also in its behaviour with reagents. By treatment with bromine it yields brom-alloxan, $C_4H_2Br_2N_2O_3$, and with nitric acid dilituric acid. The author has also examined the ammonium, sodium, and potassium salts, which are all crystallisable. The last is represented by the formula $C_5H_4KN_3O_4.H_2O$.

W. A. T.

Preparation of Parabanic Acid. By B. TOLLENS (Deut. Chem. Ges. Ber., v, 801).

THIS acid may be conveniently prepared by evaporating a mixture of uric acid with at least twice its weight of nitric acid till red crystals appear at the edges. The author has obtained a well-crystallised hydrate, $C_3H_2N_2O_3 + H_2O$.

J. R.

On a substance extracted from a Chinese Fungus. By P. CHAMPION (Compt. rend., lxxv, 1526).

AMONG the Chinese an infusion of a fungus, called by them *Fouh-ling* (*Pachyma pinetorum*), is largely used in certain venereal diseases. This fungus yields a substance, named by the author *pachymose*, which is insoluble in water, soluble in potash, and forms insoluble compounds with salts of lead and lime. Treated with warm hydrochloric acid, it reduces the potassio-tartrate of copper, and in presence of fuming nitric acid it forms a very combustible compound which detonates like gun-cotton when struck. Its composition is 32·25 C., 6·25 H., 61·50 O., corresponding to the formula $C_{10}H_{24}O_{14}$.

J. B.

Specific Gravity of Legumin and Glutin. By W. DITTMAR (Versuchs-Stationen Organ, xv, 401—403).

THE legumin was prepared from peas by Ritthausen's method; two samples were examined. Sample *a* was a bulky, very hygroscopic powder. Sample *b* was compact; it was obtained from *a* by moistening with water and drying. The glutin was prepared from wheat-flour.

The specific gravities were taken in alcohol nearly absolute. As the samples contained a little water, the gravity of the alcohol was ascertained both before and after the experiment. The specific gravities of the dry substances were found by calculation to be:—

Legumin *a*.	Legumin *b*.	Glutin.
1·360	1·285	1·297

R. W.

On Sulphophenic acid. By A. B. Prescott (Chem. News, xxvi, 269).

Note on Chloral. By E. J. Squibb (Chem. News, xxvi, 221).

On Oxy-ammonius and Phosphine-bases. By L. E. Phillips (Chem. News, xxvi, 257).

On Calabrian Manna. By Daniel Hanbury (Pharm. J. Trans. [3], iii, 421).

Physiological Chemistry.

On the use of Gelatin in Nutrition. By Carl Voit (Zeitschrift für Biologie, viii, 297—388).

The author begins this paper by a discussion of the experiments made by previous observers on the use of gelatin as food. He considers that those of Edwards and Balzac and of Magendie were vitiated by the fact that they allowed the animals on which they experimented to eat their food instead of administering it to them by force. Disgust at the gelatin prevented the dogs from eating it, and they preferred to die of hunger. Voit, however, has noticed some dogs do the same with raw meat, and others with bread. His own experiments were made by feeding dogs on gelatin and flesh, or gelatin alone, on gelatin and fat, on flesh and fat, or flesh, gelatin and fat, and observing how much flesh underwent transformation in the organism as indicated by the nitrogen excreted, and how much was lost or gained by the body. The results showed that gelatin always saves albumin, and does so to a much greater extent than fat or carbohydrates. In a large dog 168 parts of dry gelatin supplied 84 of dry flesh or albumin. An increase in the quantity of gelatin in the food was followed by a greater saving of albumin; but the saving cannot be carried beyond a certain limit, for even when the greatest possible quantity of gelatin is administered and much fat in addition, some albumin from the body or the food still undergoes decomposition. The saving effect of gelatin is greater when fat is given along with it. No permanent deposition of gelatin in the

organism takes place; but the whole of it undergoes rapid decomposition. In two days the nitrogen of all the gelatin given could be found in the urine and fæces within 24 hours, and only in one large dog were there indications that a small portion of the gelatin remained after this time, but was decomposed on the following day. This is possibly connected with the simultaneous administration of much fat, which may perhaps hinder the rapid decomposition of large quantities of gelatin. It cannot be that gelatin spares albumin by supplying the waste of gelatigenous tissues instead of letting this be done by albumin, because we must then assume that the gelatin is not completely decomposed; and if this be the case, the amount of nitrogen excreted would show that there is no saving of albumin, and no advantage would be gained. Gelatigenous tissues cannot be formed from gelatin, but, as their development shows, only from albuminous bodies. The author then gives a full account of his opinions regarding albumin in the organism. When a dog is allowed to fast for several days, the amount of albumin daily destroyed in the body will be *e.g.*, 0·8 per cent. of that contained in it. When well fed with albumin, the same dog will daily decompose 9 per cent. of albumin. This clearly shows that the relations of the albumin in the body to decomposing agencies are very different. Voit therefore divides it into (1), *circulating albumin*, or albumin in the circulating plasma or lymph; (2), *organ-albumin*. The first sort undergoes rapid decomposition. It might have been called *plasma-albumin*, but the name of circulating albumin was chosen in order to indicate that it is during circulation through the tissues that this albumin comes under the conditions of decomposition. The albumin of blood-plasma is plasma-albumin; but only a small part of it is decomposed, because the greater part of it is in a state of firmer combination as organ-albumin of the blood. Organ-albumin is not decomposed as such, for it is not subjected to the conditions of decomposition until it has undergone conversion into circulating albumin. When the equilibrium between the organ-albumin and circulating albumin is suddenly disturbed, so that the proportion of the former is increased, *e.g.*, by venesection, the excess of organ-albumin is not retained by the organism, but is converted into circulating albumin and decomposed. The author does not agree with Fick in his supposition that it is not albumin but peptones that are rapidly decomposed in the organism. Fick compares the rapid decomposition in the body which occurs after albuminous food has been taken to the blaze which occurs when a rapidly combustible body like gunpowder (to which he compares peptones) is mixed with a slowly combustible one like charcoal (which would represent albumin). Voit would rather compare it to a blaze on the addition of fine chips of wood to a burning log of the same kind. He considers the notion to be an unfortunate one that absorption in the intestine takes place by osmosis, and that albuminous bodies must, therefore, be converted into peptones before they can be absorbed. He is unable to see why it should be supposed that albuminous substances cannot pass through the intestinal walls when they readily do so through every possible membrane and organ. The albumin in the food is chiefly decomposed in the plasma current, but part of it serves to replace organ-albumin which has been destroyed, or

as a deposit. According to the doctrine of luxus-consumption also, a small quantity only of albumin is decomposed in the organs, but the replacement of this only is necessary, and any additional supply is luxus, and undergoes combustion in the blood as a surplus. According to Voit, very little albumin is decomposed during fasting, but every supply of albumin in the food increases the stream of plasma to the organs, and so much albumin is thereby subjected to the conditions of decomposition. The rich supply is not luxury (luxus), but a necessity if the body is to retain a definite amount of albumin.

The simplest explanation of the fact that gelatin, like fat and carbohydrates, cannot entirely arrest the transformation of albumin in the body is, that it cannot replace the decomposed organ-albumin or construct new organs or tissues, not even gelatigenous tissues. In this respect it behaves exactly like peptones. It lessens the conversion of organ-albumin into circulating albumin; when given alone it diminishes the loss of albumin from the organism; and when given along with albumin in food, it lessens the proportion of albumin which undergoes decomposition, so that a much smaller quantity suffices to supply the needs of the body.

Gelatin differs from other nutriments inasmuch as it cannot replace any of them; fat and carbohydrates can completely prevent the loss of fat from the body, and each inorganic constituent the loss of a similar one, but gelatin does not totally prevent the loss of albumin, but only of a part of it.

Gelatin does not lessen the loss of fat from the body to the same extent as carbohydrates, the amount of carbonic acid excreted remaining nearly the same.

When gelatin is given along with meat, it not only lessens the consumption of albumin, but also diminishes that of fat, though only to a small extent; it does not economise fat by taking up the oxygen which would otherwise oxidize it, since 200 parts of gelatin do not economise 74 parts of fat which on this supposition it ought to do, since these proportions of gelatin and fat require the same amount of oxygen for their complete oxidation.

Voit criticises Liebig's division of food into plastic and respiratory, which he considers to be quite erroneous. There is no more reason to regard albumin as plastic than water, fat and salts, for these are quite as indispensable as albumin to the constitution of a cell. Moreover, the greater part of the albumin taken into the body undergoes decomposition without even having formed part of any organ. Fat and carbohydrates, too, are not specially destined to produce heat, and they undergo decomposition quite independently of the thermal necessities of the body. It is quite a mistake to suppose that the oxygen taken in during respiration is the cause of the decomposition of the tissues, for it is in reality a consequence. The tissues split up into simple compounds quite independently of oxygen, and it is these compounds which take up the oxygen. A proper division of food can only be based on a consideration of the constituents of the body, and of what is necessary to replace the waste of these.

The constituents are water, inorganic materials, fats and albumin and its derivatives. Of water there is generally no lack, and in-

organic constituents are generally found in abundance in any diet which contains a sufficient quantity of albuminous and non-nitrogenous materials, and therefore they do not require any special consideration. Fat can be supplied by giving it directly in the food. Animals in general, and especially herbivora, cannot take a sufficient quantity in this way, and it is therefore necessary to give carbohydrates in addition, which probably do not themselves form fat, but economise it. It can also be supplied by a diet of flesh, which by decomposition in the organism, yields fat.

To replace the waste of albumin, a certain quantity of it must under any circumstances be contained in the food; at least as much as will replace the waste of organ-albumin. Generally much more than this is necessary, in order to keep up the stock of circulating albumin. A large quantity of albumin is required for this purpose when it is given alone, but much less suffices when fats and carbohydrates are given along with it, although they can never become transformed into albumin. This most important use of these articles of food was not sufficiently noticed under the old classification into plastic and respiratory. It is impossible to give gelatin a place in this classification at all, for it cannot assist in the formation of tissues, and is therefore not plastic, nor has it any greater value as respiratory food than albumin, and consequently cannot be ranked as such. Under Voit's new classification, it falls into its place at once. It economises circulating albumin, like fats and carbohydrates, but much more powerfully, in this respect resembling peptones, which are not again converted into albumin. Besides this, it economises fat to a slight extent.

T. L. B.

Dehydration in the Animal Body. By M. NENCKI (Deut. Chem. Ges. Ber., v, 890—893).

IN this paper the author maintains that it is an error to regard the animal organism exclusively as an agent of oxidation, and expresses his belief that reactions in which water is eliminated as a result of condensation and similar processes, play a very important part in animal life.

In illustration of his views, he cites a number of well-known reactions in which constituents or decomposition-products of the animal body result from the coalescence of two simpler substances, and separation of water.

W. A. T.

The Heat produced in the Body, and the Effects of Exposure to Cold. By JOHN C. DRAPER (Amer. Jour. of Science [3], iii, 445—449).

THE results were obtained in an attempt to determine the quantity of heat passing off from the surface of the body, by finding how much it would elevate the temperature of a known mass of cool water during a given period of time.

In the first series of experiments, the body was kept at rest in a

bath of cold water, the temperature of the air being 27°—28°, and that of the water 23°—24°. The heat lost in the course of one hour was enough to warm the body itself about $2\frac{1}{4}$°. In another experiment one or other of the lower extremities was alternately kept in motion during thirty minutes of the hour during which the body was immersed in the bath. Notwithstanding the violent exertion which this procedure involved, there was no increase in the amount of heat imparted to the water.

One of the consequences of the effect of cold on the body was a great reduction in the quantity of oxygen introduced into the system, and a consequent imperfect removal of carbon dioxide.

T. S.

Oxidation-product of Bile Pigment. By B. J. Stokvis (N. Repert. Pharm., xxi, 732—737).

An account is given of the spectroscopic characters of the body to which the discoverer originally assigned the name *choleverdin*, and to which Heynsius and Campbell afterwards gave the name bilicyanin. The author now also proposes the term *bilicyanin* for this substance. The spectroscopic description is obscure, doubtless on account of clerical errors; it is therefore not reproduced here.

A summary of the solubilities of the above oxidation-product in various menstrua is appended It is regarded by the author as an intermediate product formed during the oxidation of bilirubin into biliverdin by Gmelin's reaction.

T. S.

The Amount of Metamorphosis of Albumin after Blood-letting. By Voit and Bauer (N. Repert. Pharm., xxi, 729—731).

The authors find that, contrary to expectation, blood-letting increases the metamorphosis of the nitrogenous tissues, instead of lessening it. The fact observed receives, as they conceive, a rational explanation on physiological grounds.

T. S.

Hæmoglobin and Quinine. By Math. Müller (N. Repert. Pharm., xxi, 731, 732).

Quinine in neutral solution is found to restrain the ozonising property of solutions of blood and of hæmoglobin. An exceedingly small quantity (1—1,000th of quinine) sensibly diminished the power of the blood as a carrier of ozone.

T. S.

Amount of Iron contained in Blood and in Foods. By M. Bouissingault (Ann. Chem. Phys. [4], xxvii, 477—503).

The main results of this investigation have already been noticed in this *Journal* (p. 832 of last volume). In the present paper, the mode

of experimenting is fully described, and tables are given of the proportion of iron in the blood of various animals and in various articles of food.

T. S.

On the number of the Red Corpuscles in the Blood of Mammals, Birds, and Fishes. By L. Malassez (Compt. rend., lxxv, 1528—1531).

M. Malassez describes a simple method of enumerating the blood-corpuscles. It consists in making an exact mixture of a small quantity of blood (a drop suffices) with a preservative fluid in the manner recommended by M. Potain. This is introduced into a flat capillary glass tube (called an *artificial capillary*), the volume of which is calculated for each unit of length. By means of the microscope, the ocular of which is divided into squares, the number of corpuscles within a certain number of squares can be counted. The length of the tube included within the squares and the corresponding volume being known, the number of corpuscles in the cubic millimeter can be readily determined.

The number of corpuscles in the cubic millimeter is in mammals from 3,500,000 to 18,000,000. The average number in man is 4,000,000; in camels, 10,000,000 to 10,400,000; in goats, 18,000,000; in the porpoise, 3,600,000, a number exceeding that of fishes. Birds have fewer corpuscles than mammals. The maximum is 4,000,000, the minimum 1,600,000, the average being 3,000,000. Fishes possess fewer than birds, and osseous and cartilaginous fishes again differ from each other in this respect. In osseous fishes the number in each cubic millimeter is from 700,000 to 2,000,000; cartilaginous fishes have 140,000 to 230,000. This difference is remarkable when fishes having the same habit are compared, such as the turbot, &c., on the one hand, and the ray, &c., on the other.

The number of corpuscles, therefore, diminishes as the animal is lower in the scale. As, however, the richness of the blood depends, not on the mere number of the corpuscles, but also on the surface, volume, and weight of each, as well as on the quantity of hæmoglobin each contains, all these questions would have to be solved in order to estimate it.

For want of any exact method of doing so, the author confines his attention to a comparison of the number of the corpuscles with their dimensions. The corpuscles increase in size the lower in the scale, and hence there is an inverse proportion between the size and number of the corpuscles. This proportion is, however, not always constant, as man possesses fewer and yet smaller corpuscles than the dromedary and llama. As a rule, the diminution in number is compensated by increase in volume; but this compensation is not always exact, for birds gain more by the augmentation in volume than they lose by diminution in number, as it has been found that birds have heavier corpuscles than mammals.

D. F.

Composition of the Bones of Rabbits of various Ages.

By E. Wildt (Landw. Versuchs-Stationen, xv, 404—454).

Previous experimenters had shown that the various bones of an animal differ in composition, and that different parts of the same bone vary; the author, therefore, determined to compare only similar bones, and to take for his subject an animal the bones of which were small enough to admit of whole bones being operated on. The bones taken from each rabbit were the clavicula, humerus, radius, and ulna, the femur, tibia, and fibula. The periosteum was removed, the bones partially dried, and then coarsely powdered. Water was determined at 140°. Fat was extracted by ether. After removal of the fat, the powdered bone was treated three times with cold water, each digestion lasting 24 hours; the united extracts were dried and weighed, and the ash determined. The purified bone was now reduced to a fine powder. In one portion, carbonic acid was determined. Another portion was calcined, and carbonic acid again determined. The ossein was estimated from the loss on ignition, corrected for the difference between the two determinations of carbonic acid. The ash was analysed by the usual methods, fluorine being determined by difference.

Age of rabbits.	Number taken.	Bones from one rabbit (grams).	Water per cent. in fresh bones.	Percentage composition of dry bones.			
				Fat.	Cold water extract.	Ossein.	Ash.
Newly born......	6	·653	65·67	1·65	13·43	39·59	45·33
3 days..........	5	1·152	60·17	1·37	13·49	41·88	43·26
14 days	4	6·921	61·98	4·33	6·89	39·80	48·98
1 month........	4	10·772	56·11	4·38	5·22	37·11	53·29
2 months........	2	15·972	51·36	1·11	4·50	32·44	61·95
3 months........	3	29·031	51·16	3·29	3·22	30·22	63·27
4 months........	3	36·253	37·32	9·37	2·39	28·94	59·30
6 months........	2	43·261	26·73	16·79	2·02	24·14	57·05
8 months........	2	43·335	26·69	23·72	1·73	21·05	53·50
1 year	1	42·002	20·88	22·81	1·62	19·46	56·11
2 years	1	58·838	24·70	22·58	1·50	20·57	55·35
3—4 years	1	41·482	21·45	20·72	1·49	20·50	57·29

The growth of bone apparently ceases in 6—8 months after birth. The water plainly diminishes from birth to maturity, while the fat increases. The low amount of fat found at the age of two months is due to the rabbits in this case dying of disease. The cold water extract represents the contents of blood-vessels. This extract, at birth, contains 37 per cent. of ash, which increases to about 50 per cent. at maturity; the ash is chiefly alkaline salts, and included potash. The total combustible matter of the bone diminishes towards maturity, while the ash increases. Petzold, in his experiments on the bodies of mice, came to the same conclusion: he found that water diminished from birth to maturity, and that the ash increased in a greater ratio than the combustible matter. The composition of the purified bony substance is shown in the next table.

Age of rabbits.	Percentage composition of dry bone freed from fat and soluble matter.		Percentage composition of ash.				
	Ossein.	Ash.	Lime.	Magnesia.	Phosphoric acid.	Carbonic acid.	Loss.
Newly born ...	46·61	53·39	52·17	1·38	42·05	3·65	·75
3 days........	49·18	50·82	52·16	1·36	42·13	3·84	·51
14 days	44·82	55·18	52·10	1·26	42·19	3·99	·46
1 month	41·06	58·94	51·91	1·22	42·20	4·00	·67
2 months	34·37	65·63	52·10	1·09	41·64	4·52	·65
3 months	32·32	67·68	52·49	1·01	41·03	4·69	·78
4 months	31·28	68·72	52·60	1·02	40·80	4·92	·66
6 months	29·74	70·26	52·61	1·05	40·80	4·94	·57
8 months	28·23	71·77	52·78	·93	40·05	5·54	·70
1 year	25·76	74·24	52·61	·91	40·04	5·71	·73
2 years	27·10	72·90	52·76	·93	39·78	5·81	·72
3—4 years	26·35	73·65	52·84	·83	39·80	5·66	·87

The bone-ash contained no iron (here agreeing with Plugge), and only traces of soluble salts. The lime increases slightly towards maturity, and the carbonic acid increases considerably, while both magnesia and phosphoric acid diminish. Calculating the loss as due to fluorine (the presence of which the author does not establish), the calcium fluoride varied from 1·62—3·08 per cent. Assuming the existence of this fluoride, and reckoning the magnesia as trimagnesic phosphate, the author finds in every case an excess of phosphoric acid over lime; he calculates that, on an average, one part of dicalcic phosphate is present for seven parts of tricalcic, the extremes being 1 : 5·1—8·8. If we regard fluorine as absent, there still remains in every case a slight excess of phosphoric acid. The old controversy as to the composition of bone phosphates is thus revived. Berzelius, Recklinghausen, and Scherer, regard the phosphates as partly dibasic; while, according to Heintz, they are wholly tribasic. The author points out that in Heintz's analyses the carbonic acid is unusually low, and that if it be raised to the ordinary percentage for adult bone, a part of the phosphates will then become dibasic. The author believes that the expulsion of carbonic acid during the calcination of bone is due to the action of dicalcic phosphate upon the calcium carbonate; this view is supported by the fact that, notwithstanding the loss of carbonic acid, the ash of purified bone is not alkaline to turmeric, nor does it increase in weight by treatment with ammonium carbonate.

The author finally discusses the composition of brittle, unhealthy bone. According to Aeby and Reichardt, the brittle bone contains rather more carbonates; but the author's analysis of the pelvis of a hyena which had died of this disease, shows the bone to be of a normal composition, and he thinks the brittleness may be due to molecular arrangement.

R. W.

A Beetle Eudiometer—a Suggestion for a Lecture Experiment.
By W. MÜLLER (Pogg. Ann., cxlv, 455—459).

SPECIMENS of *Acilius sulcatus*, *Carabus granulatus*, and *Dyticus marginalis*, confined in a eudiometer tube containing air, over water, with a small vessel of calcium hydrate in the tube to absorb the carbonic anhydride produced, were found capable of consuming the whole of the oxygen of the air. The two first-named species lived the longest in an atmosphere of nitrogen, but the last was usually employed, being more easily obtainable.

Two experiments performed in October are given as examples. In the first 66·6 c.c. of air were contained in the tube; after 72 hours the volume became constant, and remained so for a further 22 hours, when the beetle was removed, and a diminution of 20·88 per cent. of the air was found to have occurred. In the second experiment 57·4 c.c. of air lost 20·94 per cent. of its volume in 64 hours, and after another 6 hours the beetle was removed. After the first experiment, the beetle resumed its usual activity in two days, and after the second experiment the beetle completely recovered in an hour.

Some experiments were made in June, but in these the whole of the oxygen was not removed and the beetles frequently dried, probably owing to the increased activity of their functions at this time of the year not permitting them to adapt themselves so completely to an altered atmosphere. In one experiment a small frog retained its vitality during a sojourn of six hours in pure nitrogen.

These experiments are well suited to show the revivifying power of oxygen after the insects are seemingly dead.

E. K.

Chemistry of Vegetable Physiology and Agriculture.

The Influence of Coloured Light on Assimilation by Plants.
By E. LOMMEL (Pogg. Ann., cxlv, 442—455).

THE author enumerates many of the conclusions arrived at by different experimenters on this subject, and considers it a well ascertained fact that the greatest amount of decomposition is produced by those rays which are absorbed by chlorophyll, and have at the same time a high mechanical intensity.

Solid chlorophyll shows the absorption bands ii, iii, and iv, but very much less plainly than a solution of chlorophyll, because the white light which passes between the interstices of the chlorophyll cells, usually forms a continuous spectrum over the absorption bands, and so dims or wholly obliterates the paler ones, whilst the band i suffers only a slight diminution in intensity. The theory of the author is supported by the direct experiments of N. J. C. Müller (*Botanische Untersuchungen:* Heidelberg, 1871), and by the following experiment.

Two similar bean-plants were placed in frames, the sides and top of the first of which were composed of a combination of blue cobalt glass

and red copper glass, which allowed only the red rays between A and B to pass through; in the second, a combination of red and violet glass was used, which transmitted only the middle red rays. Both combinations were so dark, that the plants could scarcely be seen from the outside; their power of transmitting heat-rays was almost identical. At the end of a week the first plant was sickly, and had not increased in size, whilst the young leaves of the second plant had doubled in size, and it was not to be distinguished from a similar plant kept in diffused daylight. This experiment shows that the middle red rays above can support the growth of a plant, whilst the outer red rays are unable; and also that assimilation is dependent on the quality of the rays, and not on the intensity of the light.

E. K.

Pressure of the Sap in the Vine. By C. NEUBAUER (Deut. Chem. Ges. Ber., v, 800).

THE author found the pressure of the sap in spring equal to a mercury-column of 40—60 centimeters. He has detected in the leaves of the vine: quercetin, quercitrin, tannin, inosite, malic, tartaric, and oxalic acids, sugar, and protein-compounds.

J. R.

Fermentation of Fruits. By G. LECHARTIER and F. BELLAMY (Compt. rend., lxxv, 1203).

FRUITS (apples, cherries, &c.) placed in a closed vessel absorb all the oxygen present, and evolve a large quantity of carbonic acid gas. A quantity of alcohol is also produced at the same time, its formation being accompanied by destruction of sugar. Apples under these circumstances exhale water-vapour, which stands in drops upon their sides, and even sometimes forms a layer at the bottom of the vessel. In five instances the alcoholic ferment was found in a budding state in the interior of the apples. In a sixth case the alcoholic ferment was not found, but in this instance the apples were enclosed in the vessel later in the season, and the vessel was opened before the usual cessation in the evolution of the carbonic acid gas had occurred. Numerous other experiments have shown that the disengagement of gas from fruits enclosed as above, takes place at two distinct periods. The first period may last several months, and then the evolution will cease for one or two months, when it will recommence, and proceed with greater rapidity than before. A destruction of sugar and production of alcohol takes place during both periods, but it is only after the second period that the alcoholic ferment is found to be present in a budding state.

In experiments on the same subject by Pasteur (*Compt. rend.*, lxxv, 1054), the fruits were plunged at once into carbonic acid gas; the formation of alcohol was then appreciable within 24 hours, and was accompanied by a sensible production of heat.

J. B.

Antiseptic Properties of Sodium Silicate. By M. PICOT (Compt. rend., lxxv, 1124).

To 50 c.c. of a solution containing 10 grams of glucose and 5 grams of yeast, were added successive quantities of sodium silicate; it was found that fermentation was retarded in proportion to the quantity of silicate added, and that 80 centigrams were sufficient to stop the fermentation altogether. Twenty centigrams of the silicate prevented the spontaneous fermentation of 50 c.c. grape juice. The salt also retards or prevents the fermentation of cane-sugar and milk-sugar according to the quantity added. Milk is also prevented from becoming acid, and solutions of animal matter from becoming putrid by the addition of a certain proportion of this salt.

J. B.

Second Observation on some Recent Communications by M. PASTEUR (C.R., lxxv, 784), *especially on the Theory of Alcoholic Fermentation:* By A. BÉCHAMP (Compt. rend., lxxv, 1519).—Relates chiefly to a question of priority.

Observations on a Communication made by M. PASTEUR *to the Academy of Sciences* (7 Oct. 1872): by A. BÉCHAMP and A. ESTER (Compt. rend., lxxv, 1523).—Relates to the function of cells as agents of fermentation under certain circumstances.

Discussion on Fermentation; by MM. PASTEUR, FRÉMY and TRECUL (Compt. rend., lxxv, 973—990).

On the Fermentation Question: by A. GAUDIN (Compt. rend., lxxv, 1206).

Analytical Chemistry.

Quick Method of Estimating Phosphoric Acid, Magnesia, and Lime. By C. HILLE (Compt. rend., lxxv, 344—348; Dingl. polyt. J., ccv, 546—551).

Two grams of the phosphate to be examined are treated at the ordinary temperature with 50 c.c. of dilute hydrochloric or nitric acid, the solution is filtered, and the filtrate treated with citric acid, and then with excess of ammonia; the phosphoric acid is then precipitated with solution of magnesium chloride in excess, whereby the precipitated ammonio-magnesium phosphate is made to subside more rapidly than it would otherwise do. The supernatant liquid is now separated from the precipitate by means of an aspiration-filter, and the precipitate is washed with ammoniacal water, which is afterwards removed by the same means. The precipitate is next dissolved by means of a few drops of nitric acid and the phosphoric acid estimated with uranium acetate solution, according to a modification of Leconte's method.

Boussingault has stated that an excess of ammonium citrate holds in solution a considerable portion of the ammonio-magnesium phosphate, the author finds that by using not more than 80 to 100 parts of citric acid to one of phosphoric acid contained in the substance, no loss is experienced.

He also finds that by adding excess of magnesium chloride, keeping the proportion of citric acid within proper limits, adding the right quantity of ammonia in excess, and not allowing the total volume of the solution to exceed a certain amount, accurate results can be readily obtained in presence of lime, iron, and alumina.

W. S.

Colorimetrical Estimation of Combined Carbon in Steel. By J. Blodget Britton (Dingl. polyt. J., ccvi, 182—185).

The author modifies Eggertz's method. He uses sixteen glass tubes, $2\frac{1}{2}$ inches long, and $\frac{1}{2}$ inch diameter, placed in a wooden stand; these tubes are filled with a mixture of alcohol and water coloured by means of burnt coffee. The solution in the first tube at the left side, corresponds in colour with a liquid containing 1 gram of iron with 0·5 per cent. combined carbon, dissolved in 15 c.c. nitric acid. The liquid in the next tube to the right corresponds with the same amount of iron, but containing ·07 per cent. combined carbon, dissolved in the same amount of nitric acid, and so on, each solution varying in colour so as to correspond with an increase of ·02 per cent. carbon.

The back of the stand is covered with thick white paper.

The sample to be tested must be obtained in fine powder, 1 gram dissolved in 15 c.c. pure nitric acid—specific gravity 1·42—with 30 c.c. water. This solution is filtered into a test-tube, 4 inches long, and of a diameter the same as that of the tubes in the stand, and the depth of colour is compared with that of the standard solution. Care must be taken that the nitric acid used is always of the strength given above, that the liquid to be tested is at the ordinary atmospheric temperature, that the testing is made soon after dissolving the sample, and that all circumstances under which the standard solutions and the solutions of the samples are made, is the same in both cases.

M. M. P. M.

Gold Assays. By H. Rossler (Dingl. polyt. J., ccvi, 185—191).

The author calls attention to the differences in the results of gold assays made by different chemists.

In estimating the gold contained in a mixture of gold and silver, a number is obtained expressing the real amount of gold minus that lost in the cupel, and plus the amount of silver retained. Are these amounts constant quantities? The amount of silver retained in gold bars prepared exactly after Kandelhardt's method, the author found to be $\frac{3}{4}$—1 milligram.

In gold bars from various sources, the amount of silver varied from $1\frac{1}{2}$—$2\frac{1}{2}$ or 3 milligrams. If, therefore, the bars are invariably prepared by one and the same method, the amount of silver retained is a constant quantity. The amount of gold lost in the cupellation process is

greater the greater the amount of lead used, and less the greater the amount of silver present. In general assays, the loss of gold is greater than the amount of silver retained.

M. M. P. M.

Detection of Water in Essential Oils. By G. Leuchs (J. pr. Chem. [2], vi, 159).

All essential oils obtained by distillation with water contain water even when they appear quite clear. The author finds that when such oils are mixed with several times their volume of petroleum-ether (the so-called benzin), a turbidity is produced, owing to the separation of globules of water, the turbidity being the more marked the greater the quantity of water present. By this means he found water in the oils of lavender, cloves, spike, cinnamon, rosemary, sassafras, and juniper; the oils of lemon and bergamot likewise contained traces of water, as did also Portugal oil and the oil of *Gaultheria procumbens*; on the other hand, the oils of turpentine, cedar, lemon, rue, and amber were found free from water.

J. R.

The Action of Crystallisable Sugar on Fehling's Solution. By E. Feltz (Dingl. polyt. J., ccvi, 384—387; from Compt. rend., lxxv, 960).

Shows, by careful experiment, that cane-sugar is capable of reducing alkaline tartrate of copper, and that the rapidity of the reduction is the greater, the larger the excess of alkali present. Two copper solutions, the one containing 0·632 grm. (a), and the other 1·34 grm. (b), Na_2O per 10 c.c., were employed, each contained in 10 c.c. as much copper as would require 0·05 grm. glucose for complete reduction. 10 c.c. of (a) were reduced by boiling 25 minutes with 1·2 grm. pure cane-sugar; while 10 c.c. of (b) took only 10 minutes under the same circumstances.

C. H. G.

Estimation of the Yield of Pure Sugar from various Raw Beet-Sugars. By C. Scheibler (Dingl. polyt. J., ccvi, 48—53; abstracted from Zeitschrift des Vereines für die Rübenzucker-Industrie, 1872—297).

The process described by Dr. Scheibler is an improved plan of carrying out the well-known method of Payen, by which the syrup adhering to the already crystallised sugar is removed by washing with an acid saturated solution of sugar in alcohol, of about 85 per cent. For Payen's single washing fluid and tared filter, Scheibler substitutes the following fluids and apparatus:—(1) Alcohol of 99—100 per cent.; (2) Alcohol of 96 per cent. saturated with sugar; (3) Alcohol of 92 per cent. also saturated; and (4) Alcohol of 85 per cent. mixed with 5 vol. per cent. of ordinary acetic acid and saturated with sugar.

About 20 grms. of the sugar to be tested is weighed into tared tubes about 2 centimeters wide and 15 centimeters long, having a narrow tube fused on to them at one end, and containing a plug of felt or cotton-wool just above the junction of the wide and narrow portions. These tubes are connected by their narrow ends with bottles in which a partial vacuum can be created by some convenient means, such as a Bunsen water-pump, while their wide upper extremities are closed by corks carrying two tubes, one of which serves for the admission of dry air, and the other (carrying a stop-cock) for the introduction of the washing fluids by means of a pipette. The sugar is first covered with absolute alcohol and left to stand for 15 minutes; this liquid is drawn off and replaced by No. 2, which is followed by No. 3 and then by No. 4. This last, which is the effective solvent of the syrup, is allowed to stand on the sugar for 15 or 20 minutes, and is then allowed to run off slowly; more is added and run off, and so on, till the sugar parts with no more colour to the liquid. The remaining portions of (4) are then displaced by the other liquids, used in reverse order, and the nearly pure sugar left is dried by passing air through it while the tube is surrounded by a metallic casing filled with steam. The weight of the residue so obtained is obviously that of the sugar which existed ready crystallised in the original specimen plus sand and other insoluble (in spirit) impurities. It is now only necessary to "polarise" this residue to determine the quantity of sugar which it contains, and so obtain all the data required to ascertain how much *crystallised* sugar was contained in *the original.*

C. H. G.

The Estimation of Juice in Sugar-beets. By FERD. JICINSKY (Dingl. polyt. J., ccvi, 387—402).

THE usual method of estimating the juice in sugar-beets is to determine the water in a portion of expressed juice, and the total water in a portion of the roots, and to reckon that all water in the latter existed as juice containing the same percentage as that expressed.

Jicinsky objects to this, and says that it leads to too high results, as part of the water of the roots is the natural moisture of the cellulose, &c.; and, moreover, that in estimating the water in each case, the loss of weight represents other bodies which are formed by decomposition of sugar, &c., and increases the first error.

He proposes to estimate the sugar in the juice and that in the root, and from these data to calculate the required number. He estimates the total sugar in the root by weighing off a portion of the pulp (½ normal weight); adding 50 c.c. water; macerating for 15 minutes; straining off the liquor into a graduated tube; adding other 50 c.c. water to the residue; again macerating for a like time, and adding this extract to the first; measuring the liquid so obtained; and estimating the sugar contained after making correction for the altered volume of the juice. No sufficient proof that this process will extract all the juice is given, nor is any method mentioned by which a fair sample of the pulp with its normal juice-contents can be taken.

C. H. G.

Contributions to the obtaining of comparable experimental results in the Commercial valuation of Raw Sugars. By C. KOHLRAUSCH (Dingl. polyt. J., ccvi, 318—329).

DEALS only with the preparation of a fair sample, the proper packing of the same in glass or tin, and finally recommends the use of 100 c.c. flasks having strangulated necks so as to render easy the preparation of exactly 100 c.c. of the solution for optical examination.

C. H. G.

Detection of Blood-spots. By J. W. GUNNING (Dingl. polyt. J., ccvi, 424).

THE spot is treated with alcohol, and the solution is mixed with ferric acetate, which precipitates the colouring matter of the blood. A precipitate is thus obtained in very dilute liquids, even in water containing a quantity of blood not sufficient to colour it.

On Soil Analyses and their Utility. By E. W. HILGARD (Amer. J. of Sci. [3], iv, 434—445; Chem. News, xxvii, 8, 17).

Examination of some samples of Ferrum reductum. By A. N. LITTLE (Pharm. J. Trans. [3], iii, 422).

Technical Chemistry.

Estimation of the Oxygen in Decarbonised Bessemer Iron before addition of Spiegeleisen; Consideration of the Mode of Action of the Spiegeleisen, &c. By A. BENDER (Dingl. polyt. J., ccv, 531—535).

THE metal under consideration was obtained as follows:—After the charge had been treated in the converter to the point at which spiegeleisen is added, it was run off into a white-hot fire-clay mould, and allowed to cool slowly, when a coarse crystalline structure was exhibited. The formation of this crystalline structure appears to be favoured by the oxygen contained in the metal. The metal appeared to be brittle under the roller, but exhibited unusual toughness and hardness under the chisel. The oxygen was determined with every possible precaution by combustion in an atmosphere of hydrogen, and was found to amount to 0·35 per cent. The effect of the addition of spiegeleisen is next numerically demonstrated as follows:—It is assumed that the Bessemer iron, before addition of spiegeleisen, contains 0·35 per cent. of oxygen, and it is to be noticed how much of this oxygen is abstracted in the metallic bath by the addition in question. The charge of 3500 kilos. lost 10 per cent. of slag, leaving 3150 kilos. of metal containing 11·02 kilos. oxygen. 325 kilos. spiegeleisen were added containing 5 per

cent. carbon and 8 per cent. manganese, *i.e.*, 16·25 kilos. carbon and 26 kilos. manganese. As 55 Mn. will saturate 16 O., 26 kilos. manganese will saturate 7·67 kilos. oxygen, leaving 3·45 kilos. oxygen. The carbon, as indeed shown by the flame at the time of addition of the spiegeleisen, likewise operates. 3·45 kilos. oxygen require 2·58 kilos. carbon, leaving 13·67 kilos. carbon. The Bessemer metal before the addition contained 0·08 per cent. carbon, equal to 2·52 kilos. carbon; afterwards it contained 16 2 kilos. carbon. The steel obtained contains only from 0·15 to 0·20 per cent. manganese, and the author considers that as the manganese and carbon of the spiegeleisen both operate together upon the oxygen, the excess of the manganese (not retained in the steel) passes away in the slag with the equivalent amount of carbon, leaving the above small quantity (0·15 to 0·20 per cent.) united with the steel. 0·15 per cent. = 5·17 kilos. manganese, and 5·17 kilos. manganese is equivalent to 1·12 kilos. carbon. 16·2 − 1·12 = about 15 kilos. carbon, or about 34·50 kilos. of metal, or the steel according to this would contain 0·43 per cent. carbon. The actual experimental result is 0·40 per cent. carbon.

From three-fourths to four-fifths of the manganese introduced into the iron are lost in the slag, and it is quite an undecided question whether the small portion which remains in the steel improves its quality or is really injurious. By the addition of spielgeleisen a slight increase of silicon and diminution of sulphur are noticed. The author attempts to show that by using a good white carburetted iron instead of spielgeleisen, an equal advantage as to quality and increased quantity would be attained.

Both these agents, however, are faulty, as the gaseous carbonic oxide formed by the action of the carbon contained in either, upon the oxygen in the Bessemer metal, appears to be partially held in solution by the fluid iron, and is liberated on solidification, the steel suffering in quality thereby. This objectionable phenomenon of "blowing" would be avoided if a substance could be found capable of uniting with the oxygen to form an easily fusible slag, instead of a gaseous product. Such a discovery made and practically carried out, would exert a considerable influence in the improvement of the quality of Bessemer steel.

W. S.

Certain Facts relating to the Bessemer process.

By F. KESSLER (Dingl. polyt. J., ccv, 436—438).

Two series of analyses of Bessemer iron in its different stages, and of the raw material, confirming the facts that the carbon does not burn till most of the silicium has been eliminated, and that the phosphorus increases relatively to the iron, owing to the combustion of the latter.

C. H. G.

The Sulphurous Impurity in Coal Gas.

By A. VERNON HARCOURT (Chemical News, xxvi, 267).

THE vapour of carbon sulphide is not removed from coal-gas by the

ordinary method of purification from sulphuretted hydrogen, and, consequently, when the gas is burned, sulphurous anhydride is produced. To get rid of this impurity, the author passes the gas (either before or after purification) through an iron tube filled with iron turnings, and heated to redness. The sulphur of the carbon sulphide is, in this manner, converted into sulphuretted hydrogen, and the total amount of carbon sulphide is so far reduced, that the gas, after purification from sulphuretted hydrogen, contains only 5 or 6 grains of sulphur instead of 30 grains in 100 cubic feet.

A somewhat greater reduction in the amount of sulphur is obtained by heating the gas after, instead of before purification, and purifying it a second time.

When coal-gas is passed slowly over red-hot iron, a soft, black carbonaceous deposit is formed, and the gas is deprived of a portion of its carbon; but if the gas be passed through more rapidly, no such deposition takes place, although the time of contact with the heated surface is sufficient to effect the conversion of the carbon sulphide into sulphuretted hydrogen.

In the latter case, no diminution in the illuminating power of the gas takes place; on the contrary, if the heat be raised to bright redness, a slight yet perceptible increase in the illuminating power may be observed. This increase in luminosity after exposure to an intense heat is remarkably shown in the decomposition of marsh-gas by the electric spark; although carbon is deposited, and the volume of the gas nearly doubled, it nevertheless burns when ignited at a jet, with a flame many times more luminous than that of the marsh-gas operated on. There is no doubt but that a small quantity of some more condensed hydrocarbon, probably acetylene, is produced.

As a lecture illustration, pure dry hydrogen may be passed over the mouth of a tube containing sulphide of carbon, and thence through a piece of combustion-tubing heated nearly to redness. The mixture of hydrogen and sulphide-vapour has no action on a solution of lead acetate, but, after the application of heat, the issuing gas produces at once a black precipitate of lead sulphide. The presence of moisture appears to facilitate this reaction.

J. W.

Effect of India-rubber Tubes on the Illuminating Power of Coal-gas. By K. Zulkowsky (Deut. Chem. Ges. Ber., v, 759—763).

Three mineralised india-rubber tubes, having a total length of 4·26 meters, were enclosed in three glass tubes which were in communication with each other and with the gas-meter of the photometrical apparatus. The gas-meter, which was so regulated as to furnish 5 cubic feet in an hour, was then supplied alternately with coal-gas which had passed over the india-rubber or with ordinary coal-gas, and the illuminating powers estimated:—

Illuminating Power of Coal Gas.

	Directly supplied.	Passed over caoutchouc.	Directly supplied.	Passed over caoutchouc.	Directly supplied.
1st series	13 2	10·7	12·9	—	—
2nd "	12 2	9·2	12 1	—	—
3rd "	—	7 8	11·2	7·5	11·3
4th "	—	9·8	11·6	9·9	12 0

The diminution of the illuminating power was thus proved to be due not to the diffusion through, but to the absorption of some of the light-giving constituents by the india-rubber. To determine the amount of this absorption, some pieces of black caoutchouc were dried in a vacuum over sulphuric acid, and then placed in a chloride of calcium tube through which perfectly dry coal-gas was passed. The increase of weight after intervals of six hours is given in the following table:—

	The weight of the india-rubber tube was	Increase of weight.
At the commencement	11 889	—
After 6 hours................	12·001	0·152
" 12 "	12·125	0·124
" 18 "	12·253	0·128
" 24 "	12·369	0 116
" 30 "	12·505	0·136
" 41 "	12·691	0·186
" 47 "	12·745	0·054
" 53 "	12 816	0·071
" 59 "	12·873	0·057
Total		1·024

When the india-rubber tubes, after several days' exposure to the current of gas, were transferred to a vacuum over sulphuric acid, the manometer rose slowly and the sulphuric acid turned black, showing that the absorbed gaseous constituents were given off again.

As the same effect must be produced by diffusion when the india-rubber tubes are exposed to the air, we understand why tubes which have been in use for a long time diminish the illuminating power quite as much as new ones.

The diminution of volume caused by the india-rubber was found to be very small, amounting to 1·1 per cent. only, but was much greater in the case of coal-gas, which had been passed over benzol, evidently because vapours are more easily absorbed than permanent gases.

R. S.

On certain Gas-liquors from Gas Works, and on the Chlorides contained in certain Coals. By G. Th. Gerlach (Dingl. polyt. J., cxxxii, 552—560).

The aqueous product of the distillation of coal which is obtained as a bye-product, with the tar, in the preparation of illuminating gas, is a liquid smelling of tar, and contains in solution certain quantities of benzene and creosote. Its commercial value depends upon the amount of ammoniacal compounds it contains, which, besides ammonium carbonate, sulphide, and thiosulphate, consist of cyanogen-compounds of ammonium, notably the sulphocyanate, some ammonium sulphate, and varying quantities of ammonium chloride. In some gas-liquors the strength in ammonia of the original liquor was found to be not nearly so great as in the distillate obtained by heating it with excess of caustic alkali or lime. In this case there must have been present an abundance of ammoniacal salts decomposible by fixed alkalis, besides volatile ammonia-products.

The author's researches have shown him that besides a little ammonium thiosulphate, there are always present in gas-liquors small quantities of ammonium sulphate, and especially ammonium chloride. Many gas-liquors, as for instance, those obtained when Zwickau coal is used, contain ammonium chloride as a chief constituent, whilst but little exists in liquors from Ruhr, Saar, or Newcastle coals, ammonium carbonate being in these cases the chief constituent. W. S.

The value of Carbon-filters in purifying Drinking Waters. By Julius Müller (Archiv. Pharm. [3], i, 385—388).

Water standing in a glass globe the mouth of which was stopped with cotton wool, showed after some days signs of vegetable growth on its surface. The same water filtered through a carbon-filter into a globe free from air, also soon showed like signs of the existence of life. The same water after boiling remained perfectly clear for days.

The author therefore concludes that carbon-filters are useful only in purifying water from mechanical impurities as sand, lime, &c., but that they cannot remove any of the so-called "germs."

M. M. P. M.

Decolorising Action of Animal Charcoal. By H. Schwarz (Dingl. polyt. J., ccv, 430—435).

The coloured solutions experimented with were a highly acid solution of indigo sulphate and a neutral solution of indigo-carmine. The indigo in each of these solutions was determined by means of a solution of permanganate before and after the absorbing action of a certain weight (10 grams) of the charcoal used, on equivalent quantities of the two liquids.

Ordinary bone-charcoal was separated into three portions by sieves, large, medium, and fine. One portion of the fine was exhausted by hydrochloric acid, washed, and air-dried. Some of the large was burnt white, and two portions of this bone-ash were moistened re-

spectively with solutions containing 10 per cent. of sugar and 14 per cent. glue, then dried and ignited out of contact with air. The charcoal was either boiled with the solution in a flask, or simply shaken with it in the cold:—

Influence of Size of Grain and of Temperature.

10 grams of bone-char absorb of acid indigo-solution:	coarse.	medium.	fine.
boiling..............	·0999	·0988	·101 gram of indigo
to 100 pts. of carbon.....	9·5	9·4	10 2 p.c. ,,
cold	·119	·1025	·1105 gram ,,
to 100 pts. of carbon.....	11·3	9 76	9·5 p.c. ,,

Influence of Acid or Neutral Reaction.

10 grams of bone-char absorb of indigo-carmine:	coarse.	medium.	fine.
boiling..............	·0202	·0256	·0426 gram of indigo
cold.................	·0677	·0720	·0126 ,,
boiling..............	1·92	2·28	4·06 } p. c. to 100 of carbon.
cold	6·45	6·86	5·72 } p. c. to 100 of carbon.

Action of Lime-free Charcoal.—Each 100 of *carbon* absorbed at boiling temperature 5·04 grams indigo from the acid solution, and 1·92 gram indigo from the neutral solution.

Action of Bone-ash.—For the solutions used it was found that the white (carbon free ?) ash had an absorption power equal to 26·8 per cent. of that of the bone charcoal from which it was derived.

Regenerated Bone-black.—10 grams regenerated with sugar absorbed from hot acid solution ·0557 gram indigo.

10 grams regenerated with sugar absorbed from cold acid solution ·0645 gram indigo.

10 grams regenerated with glue absorbed from hot acid solution ·0546 gram indigo.

10 grams regenerated with glue absorbed from cold acid solution ·0557 gram indigo.

10 grams regenerated with sugar absorbed from hot neutral solution ·0240 gram indigo.

10 grams regenerated with glue absorbed from hot neutral solution ·0196 gram indigo.

C. H. G.

Revivification of Animal Charcoal by Ammonia.

By H. Eisfeldt and C. Thumb (Dingl. polyt. J., ccv, 405—411).

The spent char is boiled with a 2 per cent. solution of ammonia several times renewed, washed and rinsed, with or without burning. Several patents having this object have been taken out in England in past years.

C. H. G.

On the Function of Sulphurous Acid when employed for the Saccharification and subsequent Alcoholisation of Grain. By V. HEMILIAN and N. MELNIKOFF (Chem. News, xxvi, 283).

WHEN sulphurous acid is used in the mashing of a mixture of malt and grain, its action is twofold; on the one hand, it perceptibly diminishes the saccharific power of the diastase present in the malt, but on the other hand, it renders the starch more fit for conversion into glucose, probably by dissolving the gluten and other albuminoid substances of the meal, and thus bringing the starch into immediate contact with the diastase. The difference, which determines the increase in the quantity of glucose, depends directly on the duration of the cold maceration, and on the quantity of sulphurous acid employed. The best results are obtained with a solution containing from 0·1 to 0·13 per cent. of the quantity of malt and meal used, and by continuing the cold maceration for five or six hours. The increase in the yield of glucose under the action of sulphurous acid in the most favourable conditions, varies from 2 to 3 per cent. of the weight of the grain employed.

This method is applied commercially as follows:—The meal, without malt, is macerated in the cold with the solution of sulphurous acid, and then heated to 50°, so as to volatilise any free acid. The malt is next added, and the mixture is well stirred and heated to 70°—75°, the temperature best suited for saccharification. During the fermentation, sulphuretted hydrogen is evolved in small quantity mixed with the carbonic acid, and some unknown sulphur-compounds are formed in the liquor. The amount of free acid produced in the wort at the expense of the alcohol is only about half that formed under ordinary conditions, and thus not only is the yield of alcohol increased, but the nutritive value of the spent wash, as food for cattle, is rendered greater.

J. B.

Dynamite. By H. SCHWARZ (Dingl. polyt. J., ccv, 429).—Dynamite, dualin, lithofracteur, &c., all consist of nitroglycerin absorbed by different substances. Two samples of the first-named were analysed.

	No. 1, strong.	No. 2, weak, for coal blasting.
Nitroglycerin	67·5	56·9
Chalk and sawdust ..	30·11	42·13
Moisture and loss	2·39	0·97

Nobel's original dynamite contains 75 per cent. nitroglycerin absorbed by infusorial earth.

C. H. G.

Rosin-oil and its Use. (Dingl. polyt. J., ccvi, 246.)—Rosin-oil is a product of the dry distillation of rosin. The apparatus used consists of an iron pot, a head-piece, a condensing arrangement, and a receiver. In the distillation, a light oil comes over first together with water. As soon as a cessation in the flow of the distillate occurs, the receiver is changed, and the heat is further raised, when a red-coloured and heavy rosin-oil comes over. The black residue remaining in the pot is

used as pitch. The light oil, called "pinoline," is rectified, and the acetic acid water passing over with it, is saturated with calcium hydrate, filtered and evaporated to dryness, and the calcium acetate obtained is employed in the manufacture of acetic acid. The rosin-oil obtained after the light oil has passed over, has a dark violet-blue colour, and is called "blue rosin-oil." The red oil is boiled for a day with water, the evaporated water being returned to the vessel; next day the water is drawn off, and the remaining rosin-oil is saponified with caustic soda lye of 36° Baume, and the resulting almost solid mass is distilled so long as oil passes over. The product obtained is rectified rosin-oil, which is allowed to stand in iron vessels, protected by a thin layer of gypsum, whereby, after a few weeks, a perfectly clear oil is obtained free from water. The oil of first quality is obtained by a repetition of the foregoing operation upon the once rectified oil. The residues of both operations are melted up with the pitch.

W. S.

Preparation of Patent Waggon Grease and Rosin-oil Soap. (Dingl. polyt. J., ccvi, 247.)—One hundred lbs. of rosin-oil and 80 lbs. of lime slaked to a powder, are agitated in an iron pot, and the mixture is heated with stirring, till a uniform paste is obtained free from lumps, and running from the stirring implement like syrup. With this rosin-oil soap, all the different varieties of patent grease are made as follows:—

Blue Patent Grease.—500 lbs. red rosin-oil are heated for one hour with 2 lbs. calcium-hydrate, and allowed to cool. The oil is skimmed off the sediment, and 10 to 12 lbs. of rosin-oil soap are stirred in till all is of buttery consistence and of blue colour.

Yellow Patent Grease is prepared by adding 6 per cent. of turmeric solution to the blue grease.

Black Patent Grease.—Lamp-black is used to produce the black colour.

Patent Palm-oil Waggon Grease.—10 lbs. of rosin-oil soap are melted with 10 lbs. of palm-oil; 500 lbs. of rosin-oil are then added, and as much rosin-oil soap to make the whole of the consistence of butter, and lastly 7 to 8 lbs. of caustic soda-lye.

Paraffin residues.—The thick oil which remains in the paraffin manufacture is used as a lubricating oil, partly on account of its cheapness and partly on account of its not soon solidifying by cold.

In order to thicken, some lead soap is melted with it. Mixtures of rosin-oil or rosin-oil soap and petroleum, with glycerin also, are often used as lubricants.

W. S.

Dyeing Straw with Aniline Green. By M. Hartmann. (Dingl. polyt. J., ccvi, 246).—The method is applicable in the case of straw for straw hats, artificial flowers, &c. The straw is first placed for some time in boiling water, then washed in cold water, and afterwards bleached in a bath containing 20 grams of chloride of lime and 7 to 9 grams of sulphuric acid. No more water is used than is necessary to work the straw about in. The straw is now rinsed in cold water, then wrung out and brought for a quarter of an hour into a solution consisting of sumach,

tartaric acid, and alum, dissolved in not too much water. About half the mordant solution is now poured off and replaced by pure water. Aniline green and picric acid are then added to the bath, so that the required tint is produced, the straw being agitated in the solution for some time.

W. S.

Use of Molybdic Acid in Colouring Silk Blue. (Dingl. polyt. J., ccv, 386.)—20 parts sodium molybdate and 20 parts sodium thiosulphate are dissolved in 250 parts water. To this solution heated to boiling, 6—8 parts ordinary hydrochloric acid are gradually added. A beautiful blue liquid is thus obtained.

M. M. P. M.

Oil-baths in the Aniline Manufacture. (Dingl. polyt. J., ccv, 386.)—A good mixture for these baths is made by thoroughly stirring up together 2 kilos. oil, and 7½ kilos. alcohol, adding 7½ kilos. water, and lastly 500 grams sulphuric acid. The mixture should have a milky appearance, and no oil-drops should appear on the surface.

M. M. P. M.

A New Glue. (Dingl. polyt. J., ccv, 389.)—Ordinary glue is dissolved in nitric ether, and a little bit of caoutchouc added. This solution forms a very strong glue, and does not get thick or pasty.

M. M. P. M.

Sugar-Lime as a Solvent for Glue. By E. Puscher (Dingl. polyt. J., ccv, 390.)—1 part sugar is dissolved in 3 parts water, ¼ part slaked lime added, the solution kept at 50°—60° R., and shaken up at intervals for several days; 3 parts glue are then added to 12—15 parts of this sugar solution. On gentle warming, the glue dissolves, the solution remaining clear on cooling. The addition of 2—3 per cent. of glycerin is useful, also a drop or two of lavender oil, to remove the strong "glue" smell. This glue has an effect upon certain colours, changing them to a considerable extent.

M. M. P. M.

Preparation of a very good Adhesive and Durable Paste. By F. Sieburger (Dingl. polyt. J., ccvi, 248).—Four parts by weight of glue are allowed to soften in 15 parts of cold water for some hours, and then moderately heated till the solution becomes quite clear. Sixty-five parts of boiling water are now added with stirring. In another vessel 30 parts of starch paste are stirred up with 20 parts of cold water, so that a thin milky fluid is obtained without lumps. Into this the boiling glue solution is poured, with constant stirring, and the whole is kept at the boiling temperature. After cooling, 10 drops of carbolic acid are added to the paste. This paste is of extraordinary adhesive power, and may be used for leather, paper, or cardboard with great success. It must be preserved in closed bottles to prevent evaporation of the water, and will, in this way, keep good for years.

W. S.

Parisian Wood Varnish. By R. GRAGER (Dingl. polyt., J., ccv, 382—383).—To prepare this varnish, which has been long celebrated, the author dissolves 1 part of good shellac in 3—4 parts of alcohol, of 92 per cent. (by volume) on the water-bath, and cautiously adds distilled water, until a curdy mass separates out, which is collected and pressed between linen; the liquid is filtered through paper, all the alcohol removed by distillation from the water-bath, and the resin removed and dried at 100°, until it ceases to lose weight; it is then dissolved in double its weight of alcohol, of at least 96—98 per cent., and the solution perfumed with lavender oil.

M. M. P. M.

Preparation of Floor Wax. By NESSLER (Dingl. polyt. J., ccv, 391).—50 grams of pearlash, 250 grams of wax, and 2 decilitres of water are heated to boiling in a dish, which is frequently agitated, until a thick fluid mass is formed, from which, upon removal from the fire, no watery liquid separates out. Boiling water is now cautiously added to the mass, until no watery drops are distinguishable. The dish is again set on the fire, but its contents are not allowed to boil, otherwise myricin would separate out, 4—4½ litres of water being added, little by little, with constant stirring. Colouring matter may be added, if desired.

M. M. P. M.

Colouring and Drying of Natural Flowers. By E. PUSCHER (Dingl. polyt. J., ccv, 391—92).—The flowers are placed in a glass funnel, which is inverted over a plate containing a few drops of sal-ammoniac solution. After a few minutes, most blue, violet, or bright carmine-coloured flowers change to a Schweinfurt green; dark carmine flowers become black, white change to sulphur-yellow. The flowers plunged into fresh water retain their new colours for 2—6 hours, and then lose them. By a somewhat similar treatment with hydrochloric acid, many flowers, especially asters, may be coloured a beautiful red, which is lasting after the flowers are carefully dried.

M. M. P. M.

Permanent Paint for Fire-proofing Wood. By F. SIEBURGER (Chem. Centr., 1872, 447).—1. The wood is twice painted over with a hot saturated solution of 1 part of green vitriol and 3 parts alum. 2. The wood, after drying, is again painted with a weak solution of green vitriol, in which pipe-clay has been mixed to the consistency of ordinary paint. This coat is renewed from time to time.

C. H. G.

Microscopic Photography. By L. ERKMANN (Zeitschr. Anal. Chem., xi, 395; Chem. Centr., 1872, 395).—For taking microscopic photographs, the author recommends that the section of the plant or other tissue be placed for a night in a solution of aniline-red, not too concentrated. On washing the tissue with water, the non-nitrogenous tissues are left uncoloured, whilst the nitrogenous tissues remain

coloured, there being also a considerable amount of shading. From a negative photography thus prepared, a positive may be obtained in which the nitrogenous substances are dark and the non-nitrogenous light.

A. P.

New Depilatory. By R. Böttger (Dingl. polyt. J., ccv, 492).—A mixture of 1 pt. by weight of sodium sulphydrate, and 3 pts. of fine chalk moistened with water and kept in well-closed bottles.

W. S.

New Process for the Utilisation of Tin Plate Cuttings. By A. Ott (Dingl. polyt. J., ccvi, 198).

Presence of Silver in Commercial Subnitrate of Bismuth. By C. Ekin (Pharm. J. Trans. [3], iii, 381).

Cheap Saline Disinfectants. By S. W. Rich (Chem. News, xxvi, 196).

Method of rendering Corks for Bottles Air-tight and Indestructible. By F. Ruschhaupt (Dingl. polyt. J., ccvi, 423). The corks are soaked in melted paraffin.

Defuselation of Crude Spirit by Wood-charcoal. By W. Schulhe (Dingl. polyt. J., ccvi, 211—234).

Sinclair's Apparatus for the conversion of Wood into Paper-pulp by Chemical means. (Dingl. polyt. J., ccvi, 255.)

Petroleum exploration in Galicia and America. By A. Fauck (Dingl. polyt. J., ccvi, 237).

Anthracene-blue. By Ferd. Springmühl (Dingl. polyt. J., ccvi, 158).

Cheap Printing-colour for Aniline colours on Cotton. (Dingl. polyt. J., 158.)

Varnish made from Ebonite cuttings. (Ding. polyt. J., ccv, 159.)

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XII.—*On Ethyl-amyl.*

By HARRY GRIMSHAW, Dalton Chemical Scholar in the Laboratory of the Owens College.

ETHYL-AMYL was first prepared by Wurtz (*Ann. Ch. Phys.* [3], liv, 278), who formed it by the action of sodium on the iodides of ethyl and amyl. He found its boiling point to be 88°, and its specific gravity 0·7069, but did not study any of its derivatives. In 1862 (*Journ. Chem. Soc.* [2], i, 425), Schorlemmer showed that by the action of chlorine it yielded a heptyl chloride, and in 1866 (*Proc. Roy. Soc.*, xiv, 168), he investigated other derivatives of this hydrocarbon, and prepared its acetate and alcohol, from the latter of which he obtained by oxidation an acid having the composition of œnanthylic acid. In a further communication to the Royal Society, he proved that the hydrocarbon heptane boiling at 99°, is not identical with ethyl-amyl.

We now know the cause of this isomerism, for Schlorlemmer has shown that the heptane from petroleum is a normal paraffin having the constitution—

$$CH_3—CH_2—CH_2—CH_2—CH_2—CH_2—CH_3,$$

whilst from the constitution of amyl alcohol (Erlenmeyer, *Ann. Chem. Pharm. Suppl.* v, 337), it follows that ethyl-amyl contains the group isopropyl, its constitution being—

$$\begin{matrix}CH_3\\CH_3\end{matrix}\!\!>\!CH—CH_2—CH_2—CH_2—CH.$$

By his recent researches on the normal paraffins (*Trans. Roy. Soc.* clxii, p. 111), Schorlemmer has further shown that, by acting with chlorine on these hydrocarbons, in addition to a primary, a secondary chloride is formed. It appeared therefore of great interest to study the action of chlorine on the other paraffins not belonging to the normal group, whose constitution is well known, and to examine carefully the oxidation-products of the alcohol derived from them.

Of these, ethyl-amyl is for obvious reasons the most suitable, and at the request of Mr. Schorlemmer I undertook an investigation of this hydrocarbon in the sense above indicated.

The high price of iodine at the time rendered it advisable to endeavour to prepare ethyl-amyl from the bromides instead of the iodides, and on experiment the yield of hydrocarbon, allowing for loss owing to the volatility of the ethyl bromide, was found to be satisfactory. The total quantity obtained was about a litre and a half.

To prepare the amyl bromide, 400 grams of amyl alcohol and 25 grams of amorphous phosphorus were placed in a tubulated retort or a flask connected with an inverted condenser. 350 grams of bromine placed in a stopcock-funnel was then gradually added, and the mixture allowed to stand over night. The liquid was then poured off from the undissolved phosphorus, if any, and distilled into a receiver containing a solution of caustic soda. The bromide was shaken up with caustic soda solution, and then with water, afterwards dried with sticks of caustic potash, and subjected to fractional distillation, the portion boiling between 118°, and 124°, being taken to prepare the ethyl-amyl. The average yield of bromide was about 600 grams, from 400 alcohol and 350 of bromine.

The ethyl bromide was prepared in the same way, the proportions taken being 450 grams of methylated alcohol once distilled, 400 grams of bromine and 40 grams of amorphous phosphorus, care being taken to keep the mass cool. Almost the whole of the bromide thus obtained on distillation from the water bath, boiled constantly at 41°.

In order to prepare the ethyl-amyl, 150 grams each of the ethyl and amyl bromides and about 50 grams of sodium were taken (there being somewhat more than an equivalent quantity of the ethyl bromide, to allow for loss owing to its greater volatility). The mixed bromides were placed in a flask connected with a long, well cooled, inverted condenser.

The sodium was added gradually so as to keep the temperature at about 20° to 25° C., which object is aided by placing the flask in an oil-bath, and surrounding this if necessary with a vessel of water. It is necessary to be particular about this point, as below this temperature scarcely any action takes place, whilst at higher temperatures the action is so violent as to occasion a loss of material; still when the action does not readily commence, as is sometimes the case, a little heat may be applied without any danger, provided there be not much sodium present. When all the sodium had been added, and all action had ceased, heat was applied to the oil-bath, and the temperature kept at about 100° for some hours, so that the liquid dropped back pretty rapidly from the inverted condenser. The condenser was then reversed and the products of the reaction distilled off. The average yield of hydrocarbons from 150 grams of amyl bromide and 150 grams of ethyl bromide was about 100 grams, consisting of 80 grams ethyl-amyl and 20 grams diamyl. However large the excess of ethyl bromide, there

was always some diamyl formed, the quantity of which varied greatly with the same proportions of the bromides, 150 grams of each, giving in one case 30 grams of diamyl and 77 grams of ethyl-amyl, and in another only 8 grams of diamyl to 92 grams of ethyl-amyl. The circumstances under which the di-amyl was formed could not be ascertained, as neither the temperature at which the reaction was carried on, nor the length of time which it occupied, was found to determine the formation. There was always also a certain quantity of ethyl bromide left undecomposed.

After having been distilled off, the mixture of hydrocarbons was allowed to stand for some weeks over sodium. It was then repeatedly rectified over sodium, and fractionally distilled. The portions boiling from 85° to 100° were then treated with strong sulphuric and nitric acids.

By the usual method of adding strong sulphuric acid and then nitric acid by degrees, it takes almost a week before all action ceases, but by proceeding as follows the action is finished in a much shorter time. About one quarter of its volume of strong sulphuric acid is added to the hydrocarbon, and allowed to stand for a few hours, with frequent agitation. The acid is then drawn off by a separating funnel, and is found to contain all the impurities, as on addition of fresh sulphuric acid and a little nitric acid, hardly any action takes place, and altogether ceases if the mixture be allowed to stand overnight.

After separation from the acids, the hydrocarbon was washed twice with about its own volume of water, and left in contact with sticks of caustic potash for forty-eight hours, after which it was again fractionally distilled with a little sodium, when all except a very small portion came over from 88° to 90°. In order to obtain the hydrocarbon as pure as possible, the portion remaining after it had been repeatedly treated with chlorine, was left in contact for a week or two with sticks of caustic potash. On distillation, the ethyl-amyl thus obtained was found to have a constant boiling-point of 90°. The following is the analysis:—

0·1746 grams ethyl-amyl gave 0·5402 grams CO_2, and 0·2460 grams H_2O.

	Percentage.	
	Calculated.	Found.
C_7......	84	84·37
H_{16}	16	15·66

Specific gravity—

Weight of bottle and ethyl-amyl at 18·4°	(1) 4·4465
,, ,, ,,	(2) 4·4468
,, ,, ,,	(3) 4·4464

Weight of bottle and water at 18°	5·1065
Weight of bottle	3·0227

which gives the specific gravity at 18·4° of 0·6833.

In order to effect the chlorination of the ethyl-amyl, about 100 grams of the hydrocarbon were placed in a flask into which chlorine, dried by sulphuric acid, was led by a tube reaching down in the flask to within about 90 millimeters of the surface of the liquid. The flask was connected with an inverted condenser, at the upper end of which were placed two washing bottles containing solution of caustic potash, to arrest any hydrocarbon that might be carried over. The chlorine was allowed to pass through the apparatus until all the air was driven out; the hydrocarbon was then placed in the flask and heat applied so as to allow the liquid to drop quickly back from the condenser.

This was continued for the whole of the day; the flask was then removed, and the unattacked hydrocarbon separated from the chlorinated products by very slow fractional distillation, another portion of the hydrocarbon being in the meanwhile subjected to the action of the chlorine.

It was found necessary, when the day was at all bright, to protect the flask from the action of the light, as the chlorine took fire and burned in the vapour of the hydrocarbon. This also took place when the light was not so strong, if the current of chlorine were allowed to pass too rapidly.

The chloride thus obtained was subjected to several fractional distillations, and the portion boiling between 140° and 150° (which formed nearly the whole quantity) was taken to prepare the acetate. It was, however, found that small quantities of more highly chlorinated products were always formed during the reaction.

The following is the analysis of the chloride thus obtained:—

(1.) 0·227 grm. chloride gave 0·221 AgCl and 0·028 Ag.
(2.) 0·5205 „ „ 0·5503 „ 0·0219 „

Calculated for $C_7H_{15}Cl$.	Found. (1)	Found. (2)
26·39 p. c. Cl.	25·7	26·15

For the preparation of the acetate, about 15 or 20 grams of the chloride, with rather less than that quantity of potassium acetate and of glacial acetic acid, were inclosed in strong glass tubes of about 25 millimeters in diameter, and heated to 200° for about six hours, or until the reaction was completed, this being shown by the ceasing of the separation of potassium chloride at the juncture of the two layers of liquid. That all the chlorine was removed was shown by burning a little of the inflammable liquid, the flame of which showed not the slightest tinge of green.

The contents of the tubes were extracted with water, and the resulting light liquid washed with water, dried over potassium carbonate (rendered anhydrous by fusion), and subjected to fractional distillation. About one-fourth of the liquid came over between 85° and 100°, and the rest from about 150° to 180°. This higher-boiling fraction was further distilled, and came over chiefly between 160° and 175°, which portion was taken to prepare the alcohol. There was also a very small quantity of a liquid boiling above 200°. On analysis the composition of the acetate was found to be as follows:—

0·1547 of the acetate gave 0·3850 of CO_2 and 0·157 H_2O.

		Percentage.	
		Calculated.	Found.
C_9......	108	68·35	67·81
H_{18}	18	11·39	11·27
O_2......	32	20·26	—
	158	100·00	

The lower-boiling liquid from the acetate (that boiling from 85° to 100°) was allowed to stand over caustic potash, and on fractional distillation, yielded heptylene having a constant boiling-point of 91° C., and a specific gravity of 0·706 at 16° C., from the following numbers:—

Weight of bottle and heptylene at 16°	— (1)	4·9955
" " "	(2)	4·4956
" and water at 16° —		5·1088
Weight of bottle		3·0227

To prepare the alcohol, enough ethyl alcohol was added to the acetate to make a clear liquid, and then an excess of caustic potash, and the whole was allowed to stand for twenty-four hours with frequent shakings. To remove the last traces of acetate, the liquid was gently heated for an hour or two with a stick of caustic potash, until the odour of the acetate had entirely disappeared. The alcohol was then washed twice with water, dried over ignited potassium carbonate, and fractionally distilled. The distillation commenced at 145°, and the highest point reached was 170°. The lowest portion was again washed to remove traces of ethyl alcohol.

By repeated fractional distillations, the liquid was separated into two portions, of the lower of which the greater part came over between 146° and 148°. The boiling-point of the higher boiling portion was found to be 163° to 165°.

As the quantity of alcohols was small, the separation could not have been complete, though it was sufficiently so to show the existence in

the liquid of the two alcohols having a considerable difference in their boiling-points. The two portions were therefore placed together for oxidation, as the different nature of the products of this oxidation would allow of a very complete separation one from the other.

For the same reasons a portion of the "mixture" of the two alcohols was taken for analysis, which yielded the following results:—

0·2142 grams of alcohol gave 0·5664 grams CO_2 and 0·2666 grams H_2O.

		Percentage. Calculated.	Found.
C_7	84	72 4	72·11
H_{16}......	16	13·8	13 83
O	16	13·8	—
	116	100·0	

Oxidation of the Alcohols.

The mixture of the alcohols was subjected to the action of an oxidising mixture of 3 parts strong sulphuric acid, 2 parts potassium bichromate, and 10 parts water (Schorlemmer, *Proc. Roy. Soc.*, cxiv, 125). The mixture was allowed to become quite cold, and added to the alcohol in small quantities at a time, any elevation of temperature being avoided by placing the containing vessel in cold water. The liquid was frequently shaken, and the oxidising mixture added until a permanent brown tinge showed that there was an excess. It was allowed to stand overnight and then distilled in a retort until most of the liquid portion had come over, the distillate consisting of an acid liquid on which floated an oily layer. The residue in the retort was filled up to the original bulk and again distilled. This was repeated once more, and then all the distillates were neutralised with sodium carbonate and distilled in a retort until all the oily liquid had come over. The residue was evaporated down to dryness on the water-bath, forming a crude sodium salt of the acid.

The crude sodium salt was decomposed by the minimum quantity of dilute sulphuric acid, and the oily acid thus formed was separated by a funnel and dried for a day or two over phosphorus pentoxide. Its boiling-point was found to be 210° to 213° (not corrected). It was a colourless oily liquid, lighter than water, possessing a peculiar and disagreeable odour.

Preparation of salts of the acid—

(1.) *Silver Salt.*—The portion of the acid which was left mixed with the phosphorus pentoxide, was diluted with a considerable quantity of water and distilled in a retort, the distillate forming an acid liquid

with a little of the undissolved acid floating on the top. This distillate was heated to boiling and carbonate of silver added until the liquid was only slightly acid; the solution was filtered whilst hot, and on cooling, the silver-salt separated out as a white precipitate, sometimes granular and sometimes flocculent. On being left to crystallise by spontaneous evaporation, the salt was obtained in minute needle-shaped crystals. The precipitate was dried by pressure between blotting-paper and then placed over sulphuric acid for twenty-four hours. In determining the silver, the salt was placed in a porcelain crucible and heated very gradually; it first melted to a dark liquid having a green metallic lustre, at the same time decomposing. The heat was increased until all the organic matter was driven off, and the residual silver heated to fusion over the blowpipe. The following is the analysis—

(1.) 0·101 Ag salt gave 0·0463 Ag.
(2.) 0·035 „ 0·0160 „

Calculated for $C_7H_{13}AgO_2$.	Found. (1)	Found. (2)
45·57 p. c. Ag.	45·84	45·71

(2.) *Barium Salt.*—A portion of the acid was boiled with a little water and nearly neutralised with barium carbonate. Neither on evaporation by heat nor over sulphuric acid could this salt be obtained in any form but as a gummy skin; and though on leaving the solution at rest for several weeks, it separated out in what seemed to be a crystalline form, the salt on analysis showed no definite composition.

(3.) *Calcium Salt.*—The barium salt was decomposed by dilute sulphuric acid and the acid distilled off. The boiling solution of this was nearly neutralised with milk of lime, filtered, and allowed to evaporate at a gentle heat. The salt was thus obtained crystallised in microscopic plates and needles, which after drying between blotting-paper, lost on heating to 160°, 9·35 per cent. of moisture, corresponding most nearly with $Ca(C_7H_{13}O_2)_2 + 2Aq$, which requires 10·78 per cent.

The following is the analysis of the salt:—

0·0652 of the salt, lost on heating to 160°, 0·0061, and the resulting 0·0591 of the dry substance gave 0·0205 of $CaCO_3$.

Calculated for $Ca(C_7H_{13}O_2)_2$.	Found.
13·42 p. c. of Ca.	13·87

The distillate from the sodium salt, containing the oily liquid was again distilled as long as oil came over, and this was repeated twice. The last distillate was saturated with potassium carbonate to bring as much of the liquid out of solution as possible. The light layer of liquid was separated and dried over fused potassium carbonate. On

distillation it was found to boil from 143° to 145°, leaving a residue of a liquid boiling above 196°.

The liquid boiling at 144° is colourless, has a faint fruity smell, and forms a crystalline compound with sodium bisulphite, which proves it to be an acetone.

Its specific gravity was found from the following numbers to be 0·8747 at 17°.

Weight of bottle and acetone at 17°	(1)	4·8548
" " "	(2)	4·8551
" and water at 17°		5·1073
Weight of bottle		3·0220

The following is the percentage of carbon and hydrogen yielded on analysis :—

0·2373 of substance gave 0·643 of CO_2 and 0·2655 of H_2O.

C_7	84	73·68	73·90
H_{14}	14	12·28	12·42
O......	16	14·04	—
	114	100·00	

Oxidation of the Acetone.—The acetone was placed in a flask with a quantity of the chromic acid mixture, and connected with an inverted condenser; it was heated gradually to boiling, and kept in ebullition for an hour or two, when the oily layer had almost disappeared and the liquid had assumed a green tint.

The liquid and unoxidised acetone were then distilled off; the right quantity of potassium bichromate and sulphuric acid was added, and the liquid heated and distilled as before. The two residues of oxidising mixture were added together and distilled with water until no acid liquid came over. All the distillates were then neutralised with sodium carbonate, and evaporated down in a retort to separate any unoxidised acetone, and then on a water-bath to dryness. The sodium salt was decomposed by a small quantity of dilute sulphuric acid and a layer of an oily acid having the odour of valerianic acid, separated out on the surface of the acid solution. The whole was distilled in a small retort until all the oily liquid had come over, and the distillate thus obtained was distilled several times in the same way, to obtain the oily acid as free from water as possible, and to separate it from the other acid in solution. The liquid was then saturated with calcium chloride to bring as much as possible of the acid out of solution, and the upper layer of liquid separated and dried over phosphorus pentoxide. The residual calcium chloride solution was again partially distilled, the distillate saturated with more calcium chloride, and a little more

of the acid thus obtained. When rendered quite anhydrous by the phosphorus pentoxide, the acid was distilled and found to boil between 173° and 176° (not corrected).

Preparation of the Salts.

(1.) The silver salt was made in the same manner as that of the œnanthylic acid, and it decomposed in the same way when heated. The following is the analysis:—

(1.) 0·050 Ag. salt, gave 0·026 of Ag.
(2.) 0·0117 „ „ 0·006 „

Calculated for $C_5H_9AgO_2$.	Found. (1)	(2)
51·67 p. c. of Ag.	52·00	51·29

The solubility of the salt was found to be 1 part in 97·4 of water at 18°, or 100 parts water at 18° dissolve 1·03 parts, for 11·4945 grams of solution at 18° gave 0·0793 AgCl and 0·0087 Ag.

(2.) The boiling solution of the acid was nearly neutralised with barium carbonate to form the barium salt; but though the liquid was left standing for some weeks, the salt could not be obtained in a crystalline form, only a sort of skin forming on the surface. The same took place on evaporating down by heat, or over sulphuric acid.

(3.) As the barium salt would not crystallise, it was decomposed by dilute sulphuric acid, the acid distilled off, and the solution, after heating, neutralised with calcium hydrate, to form the calcium salt. On cooling, this salt separated out in small, short, colourless needles. On evaporation by heat, the salt separated out in the form of a gummy skin on the surface, but on cooling, this skin became brittle, and assumed the same crystalline form. A portion of the solution having been left for about a week in a small test-tube, the salt separated out in a beautiful, arborescent form, on the side of the tube. The salt was dried between blotting-paper, and analysed.

0·0705 grams dried at 160°, lost 0·007 grams., and gave 0·027 $CaCO_3$.

The moisture lost was 9·93 per cent., corresponding to $Ca(C_5H_9O_2)_2$. $1\frac{1}{2}$Ag., which contains 10·04 per cent.

Calculated for $Ca(C_5H_9O_2)_2$.	Found.
16·53 p. c. of Ca.	17·00

The residue from the valerianic acid was distilled as nearly to dryness as possible; the distillate being an aqueous liquid, having an acid reaction, and the odour and taste of acetic acid. To concentrate the acid, the liquid was repeatedly distilled to a small bulk, and the strongly

but towards the end of the distillation the thermometer always rose to 92°, even if the portion boiling below 90° was collected separately, whilst of the higher-boiling fraction, a certain quantity always distilled below 90°; Warren found the boiling-point at 90·4°.

The derivatives of this hydrocarbon were prepared in the same way as those of the normal paraffins and of ethyl-amyl; the result was that, as in the case of the latter hydrocarbons, primary and secondary compounds were formed, from which the alcohols could be approximately separated.

The following table contains the boiling points of these compounds, compared with the corresponding derivatives of ethyl-amyl:—

		Derivatives of the hydrocarbon from petroleum.	Derivatives of ethyl-amyl.
C_7H_{16}		89·5°—90°	90°
C_7H_{14}		90°—92°	91°
$C_7H_{15}Cl$		144°—158°	140°—150°
$\left.\begin{matrix}C_7H_{15}\\C_2H_3O\end{matrix}\right\}O$		160°—185°	160°—175°
$\left.\begin{matrix}C_7H_{15}\\H\end{matrix}\right\}O$	Primary	165°—170°	163°—165°
	Secondary	148°—150°	146°—148°
$C_7H_{14}O$		142°—146°	143°—145°
$C_7H_{14}O$		209°—213°	210°—213°.

The acid $C_7H_{14}O_2$ boils at the same temperature as iso-œnanthylic acid, and has a very similar smell; its salts also resemble the corresponding iso-œnanthylates.

The *silver salt* is a flocculent crystalline precipitate, yielding the following analytical results:—

(1) 0·1801 gave 0·0818Ag. = 45·42 per cent.
(2) 0·0719 gave 0·0327Ag. = 45·48 ,,
Calculated for $C_7H_{13}AgO_2$ = 45·57 ,,

The *barium salt* does not crystallise, but forms an amorphous mass, like barium iso-œnanthylate.

The *calcium salt* separated, on evaporating its solution by heat, as an amorphous pellicle, but by spontaneous evaporation it was obtained in long, transparent needles or prisms.

The *ketone* $C_7H_{12}O$, boils at the same temperature as methyl-amyl ketone, and smells very like the latter compound; but on oxidising it, a marked difference between the two compounds was observed, inasmuch as the acetone from petroleum did not yield a trace of valerianic acid, the products of oxidation possessed a pure sour smell, and on decomposing the sodium salt prepared from it, not the least trace of an oily acid separated out.

Another portion of the sodium salt was therefore decomposed with

an insufficient quantity of sulphuric acid, and the liberated acid distilled off; on repeating this process, the acid was separated in four fractions, which were converted into the silver salts by boiling the distillate with silver carbonate :—

1st fraction. Small, white needles; 0·2085 gave 0·1338 = 64·17 per cent. Ag.

2nd fraction. Small, white needles; 0·0575 gave 0·0375 = 65·22 per cent. Ag.

3rd fraction. Flat, shining needles; 0·3629 gave 0·2335 = 64·34 per cent. Ag.

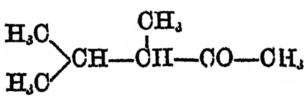
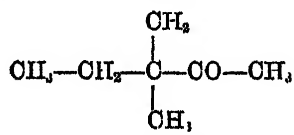
4th fraction. Flat, shining needles; 0·0800 gave 0·0515 = 64·37 per cent. Ag.

Calculated for silver acetate = 64·67 per cent. Ag.

In order to convince myself that really no other acid but acetic acid was formed, I crystallised the remaining larger portion of the sodium acetate from water and distilled the mother-liquor with so much sulphuric acid, that only a small fraction of the acid was liberated. The silver salt obtained from the distillate crystallised in small, white needles, consisting of pure silver acetate, as the following analysis shows :—0·3436 left on ignition 0·222 of silver, or 64·61 per cent.

The question now arises, what is the constitution of an acetone having the composition $C_7H_{14}O$, and yielding on oxidation only acetic acid.

From Popoff's researches (*Ann. Chem. Pharm.*, 161, 285) it follows that there may exist two ketones giving this result, viz. :—

For this chemist has shown that, on oxidising a ketone, the more stable alcohol radical always remains combined with the carboxyl, while the other radical is oxidised exactly as its alcohol would be.

The first of these two ketones will therefore in the first instance be resolved into acetic acid and methyl-isopropyl ketone, and the latter will yield by further oxidation acetic acid and dimethyl ketone, which will finally be also oxidised to acetic acid.

The second of these two ketones must, according to Popoff's law, yield acetic acid, and the oxidation-products of tertiary amyl. But the latter consist also only of acetic acid: for Butlerow has shown that on oxidising a tertiary alcohol the most simple radical always remains combined with the carbon-atom by which the whole group is kept together, whilst the two other radicals are oxidised separately, and

experiment has proved that tertiary amyl alcohol, or dimethyl-ethyl carbinol, is oxidised completely to acetic acid.

The first of the ketones is a derivative of *methyl-ethyl-isopropylmethane*, $CH\begin{cases} CH_3 \\ C_2H_5 \\ CH(CH_3)_2 \end{cases}$, a paraffin which is not yet known; whilst the second ketone is derived from *dimethyl-diethylmethane* or *carbodimethyldiethyl*, $C\begin{cases} (CH_3)_2 \\ (C_2H_5)_2 \end{cases}$, which compound Friedel and Ladenburg prepared by the action of zinc ethyl upon methylchloracetol, $CH_3—CCl_2—CH_3$ (*Ann. Chem. Pharm.*, 142, 310).

For the present it is impossible to decide with which of these two paraffins that occurring in petroleum is identical. The small quantity of ketone which I had at my disposal did not allow me to isolate the intermediate products of oxidation, the study of which would certainly elucidate the constitution of the ketone, and thus also that of the paraffin. As soon as I am able to obtain a larger quantity of the hydrocarbon, I shall endeavour to solve this question.

The properties of my hydrocarbon agree, if not completely, yet sufficiently, with those of dimethyl-diethylmethane, to make their identity not improbable. The latter paraffin boils at 86°—87°, and has at 20·5° the specific gravity 0 6958, whilst the hydrocarbon from petroleum boils at 89·5°—90°, and has at 16° the specific gravity, 0·709. The higher boiling-point which I have observed is caused, partly at least, by an admixture of normal heptane, boiling at 98°. This is the more probable, as, on oxidising the ketone, a small quantity of a liquid boiling at 149°—152°, which is the boiling-point of methyl-pentyl ketone, was left behind, this ketone being a more stable compound than the one which boils at the lower temperature.

But whatever the constitution of the hydrocarbon from petroleum may be, one thing is certain, *it is not identical with ethyl-amyl.*

Of the nine isomeric hydrocarbons C_7H_{16}, which, according to theory, can exist, we know now the following:—

Normal heptane	C_7H_{16}.
Dimethyl-butylmethane, or ethyl-amyl..	$CH\begin{cases} (CH_3)_2 \\ C_4H_9. \end{cases}$
Triethylmethane	$CH(C_2H_5)_3$.*
Dimethyl-diethylmethane	$C\begin{cases} (CH_3)_2 \\ (C_2H_5)_2. \end{cases}$

On decomposing the chlorides obtained from normal heptane with potassium acetate, I obtained some heptene boiling at 98°—99°, which I intended to use for the preparation of pure secondary heptyl-com-

* Ladenburg, Deut. Chem. Ges. Ber., v, 572.

pounds. For this purpose I added it to a large excess of fuming hydrochloric acid and left them together for several weeks, the mixture being frequently shaken. On examining the product thus obtained, I found that a little less than half of the heptene had combined with hydrochloric acid in the cold. The unaltered heptene was again left in contact with hydrochloric acid, but no combination took place even after standing for many weeks; but on heating the mixture in sealed tubes to 120°, a heptyl chloride boiling at 149°—150° was formed, whilst the chloride produced in the cold had no constant boiling point, as it always decomposed when distilled, with evolution of hydrochloric acid, the greater portion however boiling at about 140°.

The chlorides were again converted into the olefines by heating them with alcoholic potash. Both heptenes boiled again at about 98°, but besides the olefines other compounds had been formed, consisting probably of ethyl-heptyl ethers.

On treating the heptene boiling at 90°—91° with cold hydrochloric acid, I found that by far the greater portion of this hydrocarbon combines readily with cold hydrochloric acid, whilst of the heptene from ethyl-amyl, Mr. Grimshaw has observed only that a little more than one half combines with this acid in the cold, forming a heptyl chloride boiling at 134°—137°.

We have thus a means for separating isomeric olefines; a similar observation has already been made by Le Bel, who found that the petroleum from Pechelbronn in Alsace, contains two pentenes or amylenes, one combining with hydrochloric acid in the cold, and the other only at a higher temperature; also two hexenes showing the same difference (*Compt. rend.*, 75, 267).

I intend to study the action of cold and hot hydriodic acid on olefines derived from paraffins, and to convert the secondary iodides thus formed, or the chlorides, into the alcohols, the oxidation-products of which will throw further light on the constitution of the hydrocarbons of these two series.

XIV.—*On the Vanadates of Thallium.*

By Thomas Carnelley, B. Sc., Dalton Scholar in the Laboratory of the Owen's College.

The alkaline vanadates have been shown by Prof. Roscoe to differ in their chemical deportment from the corresponding phosphates, inas-

much as in the former series the meta- and pyro-salts are more stable than the ortho-salts, whilst in the phosphates this order of stability is reversed. From the high combining weight of thallium it appeared not improbable that an examination of the vanadates of this metal would throw further light upon these differences between phosphorus and vanadium.

The thallium phosphates have already been fully described by Lamy (*Ann. Chim. Phys.* [4], 5, 410). They closely resemble the alkaline phosphates both in physical and chemical characters, forming ortho-, pyro-, and meta-salts, several of which contain basic hydrogen; they are soluble in water, and the order of stability appears to be the same as in the corresponding alkaline salts. The thallium vanadates on the other hand do not, as the following experiments show, so closely resemble the alkaline vanadates, for whilst these latter are soluble in water, the corresponding thallium salts are insoluble, more closely resembling the vanadates of silver and lead.

The tendency of the vanadates to form anhydro-salts containing a greater portion of vanadium than corresponds to the ortho-compounds, is, as might be expected, even more strikingly exhibited by the thallium vanadates than by those of the alkaline metals. Thus the ortho-thallium vanadate cannot be obtained by precipitation of thallium sulphate and orthosodium vanadate, as in the cold a yellow precipitate of pyrovanadate $Tl_4V_2O_7$ falls down at once, and the solution becomes strongly alkaline. Indeed, if the above solution be precipitated when hot, a still further separation of base occurs, and a thallium vanadate having the composition $Tl_{12}V_8O_{26}$, and corresponding to one of the well known phosphates of Henneberg and Fleitmann is obtained, whilst under other circumstances another anhydro-salt, having the formula $Tl_{12}V_{10}O_{31}$, and corresponding to the other phosphate of Henneberg and Fleitmann can be prepared. A third anhydro-salt containing still less base than either of the above, and having the composition $Tl_{12}V_{14}O_{41}$, is likewise obtained by adding thallium sulphate to a solution of ammonium metavanadate.

The following investigation contains a description of the properties and mode of preparation of the thallious vanadates, with an examination of the reactions by which they are severally formed.

Method employed for the Separation and Estimation of Thallium and Vanadium.—The substance is dissolved in 4 or 5 drops of strong sulphuric acid, then diluted with water, and the thallium is precipitated by potassium iodide, a drop or two of sulphurous acid having been previously added to prevent the separation of iodine. The yellow precipitate of thallious iodide is brought on to a weighed filter, washed with alcohol, dried at 115° and weighed. The filtrate from the thallium iodide containing the vanadium is evaporated to dryness, ignited in a platinum

crucible, fused with sodium carbonate, and the fused mass dissolved in water, evaporated to a small bulk, and ammonium chloride added to saturation, the whole being allowed to stand over night. The ammonium metavanadate is then filtered, and the precipitate is washed, first with a saturated solution of salammoniac and then with pure alcohol, dried, incinerated, ignited, and weighed as V_2O_5; to oxidise the whole of the vanadium a drop of nitric acid may be added. To check this method the following experiments were made with weighed quantities of thallium chloride and vanadium pentoxide:—

	Found. (1)	Found. (2)	Calculated.
Thallium	85·17 p. c.	85·36 p. c.	85·17 p. c.
Vanadium	99·37 „	99·62 „	100·00 „

Thallium Orthovanadate, Tl_3VO_4, or *Tetravanadate*, $Tl_{12}V_4O_{16}$.—In order to prepare thallium orthovanadate, 3 molecules of Tl_2CO_3 are fused with 1 of V_2O_5, thus:—

$$3Tl_2CO_3 + V_2O_5 = 2Tl_3VO_4 + 3CO_2.$$

Great care must be taken in the fusion that the temperature be not raised too high, for the salt is easily decomposed, a small portion of the thallium being volatilised: it is best to fuse the mixture over a Bunsen's burner until it attains a dull red heat, and all the carbon dioxide is given off. On cooling, the fused mass, which is insoluble in water, is of a red colour, but on powdering becomes light brown.

In one preparation 0·708 grm. of V_2O_5 were fused with 5·444 grms. of Tl_2CO_3, the weight of CO_2 which was liberated being 0·559 grm., while that required by calculation was 0·512; the excess of 0·047 grm. obtained was probably owing to a small portion of the thallium being volatilised.

The Analyses of Thallium Orthovanadate—

(1.) Wt. of salt taken = 0·5065 grm.
Wt. of TlI obtained = 0·686 grm.; p. c. of Tl = 83·47 .... = 86·74 p. c. of Tl_2O
Wt. of V_2O_5 obtained = 0·0702 grm.; p. c. of V = 7·78 .... = 13·86 p. c. of V_2O_5

100·60

(2.) Wt. of salt taken = 0·4105 (of another preparation).
Wt. of TlI obtained = 0·557 grm.; p. c. of Tl = 83·62 .... = 86·90 p. c. of Tl_2O
Wt. of V_2O_5 obtained = 0·0460 grm.; p. c. of V = 6·30 .... = 11·21 p. c. of V_2O_5

98·11

The mean of these two analyses is as follows, corresponding to the formula Tl_3VO_4.

	Calculated.		Found. (1)	Found. (2)	Mean.	Difference.
Tl_3	= 612·0	84·03	83·47	83·62	83·55	− 0·48
V	= 51·3	7·05	7·78	6·30	7·04	− 0·01
O_4	= 64·0	8·95	—	—	—	—
	727·3	100·00				

Thallium orthovanadate cannot be prepared by precipitation, for on adding a solution of Tl_2SO_4 to a cold solution of Na_3VO_4, thallium orthovanadate is not produced, but in place of it a light yellow precipitate of the normal pyro-salt $Tl_4V_2O_7$, the liquid becoming strongly alkaline.

Thallium orthovanadate is of a light brown colour; its spec. grav. at 17° is 8·6; it is only slightly soluble in water, although it is by far the most soluble of the thallium vanadates; the following solubilities for this salt were obtained:—

1 part of salt dissolves in 999 parts of water at 15°
„ „ 574 „ 100°

Thallium Pyrovanadate, $Tl_4V_2O_7$ or *Hexvanadate*, $Tl_{12}V_6O_{21}$ is prepared—

(A.) By adding Tl_2SO_4 to a *cold* solution of sodium orthovanadate.
(B.) By fusing 2 molecules of Tl_2CO_3 with 1 of V_2O_5.
(C.) „ 2 „ „ $Tl_{12}V_8O_{26}$.

The following are the details of the three methods:—

(A.) The sodium orthovanadate is dissolved in as small a quantity of *cold* water as possible, and a cold solution of thallium sulphate added till a precipitate ceases to be formed; the latter is dense and cream-coloured, and settles easily; it is then washed with water and dried at 100° C. The filtrate has a strongly alkaline reaction.

Note.—The solubilities of the thallium vanadates were determined at 100°, by boiling a known weight of the salt with a known weight of water for known time, filtering, and weighing the insoluble residue; this subtracted from the weight taken gave the weight of salt dissolved in the known weight of water at 100°; as a check, the filtrate was evaporated to dryness in a platinum dish, and weighed. The determination for the temperature of the air was made by boiling a little of the salt with a known volume of water, cooling, filling to a mark on the vessel, which indicated the volume of water taken in order to replace that lost by evaporation. The temperature was noted and the liquid filtered; the filtrate was then evaporated to dryness, dried at 120°, and the residue weighed; this weight was that of the salt dissolved in the known weight of water.

(*a*.) Analysis of preparation (1)—

Wt. of salt taken = 0 2565 grm.; TlI obtained = 0·3275 grms.; per cent. of Tl = 78·64.

(*b*.) Analysis of preparation (2)—

Wt. of salt taken = 0·308 grm.; TlI obtained = 0·3955 grms.; per cent. of Tl = 79·14.

(B.) By fusing 2 molecules of Tl_2CO_3 with 1 of V_2O_5.

$$2Tl_2CO_3 + V_2O_5 = Tl_4V_2O_7 + 2CO_2.$$

0·8435 grm. of V_2O_5 on fusing with 4·324 grm. of Tl_2CO_3 lost 0·455 grm. of CO_2, the calculated loss according to the above equation being 0·4065 grm.; diff. = 0·0485 grms. The analysis of the salt thus obtained gave—

(*c*.) Wt. of salt taken = 0·271 grm.; TlI obtained = 0·350 grm.; per cent. of Tl = 79·59.

(C.) By fusing 2 molecules of Tl_2CO_3 with 1 of $Tl_{12}V_8O_{26}$.

$$2Tl_2CO_3 + Tl_{12}V_8O_{26} = 4Tl_4V_2O_7 + 2CO_2.$$

The fusion was carried on in a platinum crucible over a Bunsen's burner until the salt attained a dull red heat, and all the carbon dioxide was given off. After the mass had been in tranquil fusion for a few seconds, it was allowed to cool, and on cooling it yielded a light yellow powder.

4·2475 grms. of $Tl_{12}V_8O_{26}$ fused with 1·214 grm. of Tl_2CO_3, lost 0·129 grms. of CO_2, the calculation for the above equation being 0·1141 grm. of CO_2; diff. = 0·015 grm. The analyses of the salt obtained by this method gave—

(*d*.) Preparation (1.) Wt. of salt taken = 0·198 grm.

TlI obtained	= 0·254 grm.;	p. c. Tl	= 79.06	= 82·16	p. c. Tl_2O
V_2O_5 ,,	= 0·034 ,,	,, V	= 9·65	= 17·17	,, V_2O_5
				99·33	

(*e*.) Wt. of salt taken = 0·3015 grm.

TlI obtained	= 0·3855 grm.;	p. c. Tl	= 78·80	= 81·89	p. c. Tl_2O
V_2O_5 ,,	= 0·0470 ,,	,, V	= 8·74	= 15·59	,, V_2O
				97·48	

(*f*.) Weight of salt taken = 0·3625 grm. of Prep. (2).

TlI obtained	= 0·4650 grm.;	p. c. Tl	= 79·06	= 82·16	p. c. Tl_2O
V_2O_5 ,,	= 0·0635 ,,	,, V	= 9·84	= 17·52	,, V_2O_5
				99·68	

The mean of these analyses is as follows, corresponding to the formula $Tl_4V_2O_7$:—

	Calculated.		Found.						Mean.	Difference.
			Method A.		Method B.	Method C.				
			(a.)	(b.)	(c.)	(d.)	(e.)	(f.)		
Tl_4 =	816·0	79·17	78·64	79·14	79·59	79·06	78·80	79·06	79·05	−0·12
V_2 =	102·6	9·95	—	—	—	9·65	8·74	9·81	9·41	−0·54
O_7 =	112 0	10·88	—	—	—	—	—	—	—	—
	1030·6	100·00								

In order to examine the decomposition which takes place when sodium orthovanadate is precipitated by thallium sulphate 0·9545 grm. of sodium orthovanadate were dissolved in a very small quantity of cold water and a standard solution of thallium sulphate (5 grms. to $\frac{1}{4}$ litre), added from a burette till no further precipitate was formed; the thallium sulphate required = 131 c.c. = 2·62 grms.; the precipitate was washed, dried, and weighed; the weight obtained = 2·524 grms. The alkaline filtrate was titrated with standard hydrochloric acid (1 c.c. = 0·04 grms. of NaHO); the hydrochloric acid required = 4·8 c.c. = 0·192 grms. of NaHO.

This gives the following proportions:—

$$Na_3VO_4 = \frac{0{\cdot}9545}{184{\cdot}3} = 0{\cdot}00518 \quad 2$$

$$Tl_2SO_4 = \frac{2{\cdot}62}{504} = 0{\cdot}00519 \quad 2$$

$$Tl_4V_2O_7 = \frac{2{\cdot}524}{1028{\cdot}6} = 0{\cdot}00245 \quad 1$$

$$NaHO = \frac{0{\cdot}192}{40} = 0{\cdot}00480 \quad 2$$

Hence the decomposition is represented by the following equation:—

$$2Tl_2SO_4 + 2Na_3VO_4 + H_2O = Tl_4V_2O_7 + 2Na_2SO_4 + 2NaHO.$$

This result confirms the conclusions previously arrived at (Roscoe, *Phil. Trans.* 1870, page 324), inasmuch as sodium orthovanadate has been shown to be an unstable compound, easily decomposing on standing or boiling into sodium pyrovanadate and caustic soda.

Thallium pyrovanadate is a light yellow or cream-coloured powder, the specific gravity of that obtained by precipitation being 8·21 at 18·5°, while the specific gravity of that prepared by fusion is 8·812 at the same temperature. It is only slightly soluble in water.

1 part of salt dissolves in 4996 parts of water at 14°.
1 „ „ „ 3840 „ „ 100°.

On attempting to prepare this salt by precipitating a cold solution of sodium pyrovanadate ($Na_4V_2O_7 + 18H_2O$) with Tl_2SO_4, a yellow precipitate was obtained, which on analysis gave a composition intermediate between $Tl_4V_2O_7$ and $Tl_{12}V_8O_{26}$.

If, however, a *boiled* solution of sodium pyrovanadate be precipitated by thallium sulphate, a salt having the composition $Tl_{12}V_8O_{26}$ is always obtained.

β-Thallium Vanadate or *Octo-Vanadate*, $Tl_{12}V_8O_{26}$.—This salt can be prepared as follows:—

(A.) (*a.*) By adding a solution of Tl_2SO_4 in exact sufficiency or in excess to a *boiled* solution of either crystallised or fused normal sodium pyrovanadate.

(*b.*) By adding a boiled solution of normal sodium pyrovanadate in large excess to a solution of thallium sulphate.

(B.) By adding thallium sulphate to a solution of sodium octovanadate.

(A.) The normal sodium pyrovanadate was dissolved in water, the solution heated to boiling, and cooled. A cold solution of thallium sulphate was then added till no further precipitate was formed. The latter was at first quite white and curdy, like silver chloride; but in a little time and on stirring, it became yellow, very fine, and much less bulky; it was washed with cold water, thrown on a filter, and dried at 120°. The filtrate was strongly alkaline, and contained caustic soda. The precipitate contained no water, as on heating a freshly prepared sample first at 100° and then at 120°, no loss was sustained.

The salt prepared by method A, under the several circumstances, gave the following analytical results:—

Preparation (1). By adding an exact sufficiency of thallium sulphate to a boiled solution of crystallised sodium pyrovanadate—

(*a.*) Wt. of salt taken = 0·137 grm.
Wt. of TlI obtained = 0·1655 grm.: ∴ p. c.
Tl = 74·45 .... = 77·37 p. c. Tl_2O
Wt. of V_2O_5 obtained = 0·0300 grm.; ∴ p. c.
V = 12·30 .... = 21·89 p.c. V_2O_5
99·26

Preparation (2). Obtained in same way as (1).

(*b.*) Wt. of salt taken = 0·3775 grm.

TlI obtained =	0·458 grm.;	p. c. Tl =	74·77 =	77·70 p. c. Tl_2O
V_2O_5 „ =	0·0845 „	„ V =	12·46 =	22·38 „ V_2O_5
				100·08

(*c.*) Wt. of salt taken = 0·407 grm.; TlI obtained = 0·493 grm.; p. c. of Tl = 74·65 = 77·57 p. c. of Tl_2O.

Preparation (3) ditto.

(*d.*) Wt. of salt taken = 0·4025 grm.

TlI obtained = 0·482 grm.; p. c. Tl = 73·80 = 76·69 p. c. Tl_2O
V_2O_5 „ = 0·0945 „ „ V = 13·18 = 23·47 „ V_2O_5

100·16

(*e.*) Wt. of salt taken = 0·316 grm.

TlI obtained = 0·381 grm.; p. c. Tl = 74·30 = 77·22 p. c. Tl_2O
V_2O_5 „ = 0 069 „ „ V = 12·27 = 21·84 „ V_2O_5

99·06

Preparation (4). By adding an exact sufficiency of thallium sulphate to a boiled solution of fused sodium pyrovanadate—

(*f.*) One analysis was made and the percentage of Tl obtained = 73·66.

Preparation (5). By adding a large excess of thallium sulphate to a boiled solution of fused sodium pyrovanadate—

(*g.*) Wt. of salt taken = 0·231 grm.

TlI obtained = 0·278 grm. = 74·17 p. c. Tl

Preparation (6). By adding a boiled solution of fused sodium pyrovanadate in large excess to a solution of thallium sulphate—

(*h.*) Wt. of salt taken = 0·2795 grm.; TlI obtained = 0·337 grm. = 74·31 p. c. Tl.

B. According to this method the β thallium vanadate is prepared by adding a solution of thallium sulphate to a solution of sodium octovanadate. The filtrate in this case was quite neutral. The analysis of the salt prepared thus gave—

(*i.*) Wt. of salt taken = 0·377 grm.

TlI obtained = 0·453 grm. = 74·05 p. c. Tl

The mean of the above analyses is as follows:—

	Calculated.		Found.									
			Prep. (1).	Prep. (2).		Prep. (3).		Prep. (4).	Prep. (5).	Prep. (6.)	Prep. (7).
			(*a.*)	(*b.*)	(*c.*)	(*d.*)	(*e.*)	(*f.*)	(*g.*)	(*h.*)	(*i.*)
Tl_{12} =	2448·0	74·76	74·45	74·77	74·65	73·80	74·30	73·66	74·17	74·31	74·05
V_8 =	410·4	12·53	12·30	12·46	—	13·18	12·27	—	—	—	—
O_{26} =	416·0	12·71	—	—	—	—	—	—	—	—	—
	3274·4	100·00									

	Mean.	Difference.
Tl_{12} =	74·24	− 0·52
V_8 =	12·55	+ 0·02
O_{26} =	—	—

β Thallium vanadate or octovanadate corresponds with the sodium phosphate ($Na_{12}P_8O_{26}$) of Henneberg and Fleitmann (*Ann. Chem. Pharm.*, lxv, 304), and (Uelsmann, *Ann. Chem. Pharm.*, cxviii, 99). It is a fine yellow powder, the shade being darker than that of the hexavanadate; its specific gravity at 17·5° C. is 8·59. It is not decomposed at 120°, and is only very slightly soluble in water.

1 part of the salt dissolves in 3406 parts of water at 14°
1 " " " 3533 " " 100°

Decomposition which takes place on adding thallium sulphate to a boiled solution of sodium pyrovadanate—

1·0964 grm. of crystallised sodium pyrovanadate was dissolved, and the solution boiled. It was then precipitated by a standard solution of thallium sulphate (5 grms. to ¼ litre) from a burette till no further precipitate was formed. Amount of thallium sulphate used = 66·0 c.c. = 1·323 grms. The precipitate was filtered off, and the caustic soda in the filtrate determined with standard decimal hydrochloric acid; decimal acid required = 16·6 c.c. = 1·66 c.c. of real acid (1 c.c. = 0·0365) = 0·06059 grm. of HCl = 0·0664 grm. of sodium-hydrate. The calculated quantity according to the equation given below = 0·0696 grm. sodium hydrate.

This gives the following proportions :—

$$
\begin{array}{lcl|c|}
(Na_4V_2O_7 + 18H_2O) = \dfrac{1\cdot0964}{630\cdot6} & = & 0\cdot00173 & 4 \\
Tl_2SO_3 = \dfrac{1\cdot323}{504} & = & 0\cdot00262 & 6 \\
NaHO = \dfrac{0\cdot0664}{40} & = & 0\cdot00166 & 4
\end{array}
$$

∴ The equation which represents the decomposition is as follows :—

$$6Tl_2SO_4 + 4(Na_4N_2O_7 + 18H_2O) = Tl_{12}V_8O_{26} + 6Na_2SO_4 + 4NaHO + 16H_2O.$$

Decomposition which takes place on adding thallium vanadate to sodium octovanadate—

A known weight of sodium octovanadate ($Na_{12}V_8O_{26}$ + $12H_2O$) was dissolved, boiled, and precipitated, as in the previous case, with a standard solution of thallium sulphate, till no further precipitate was formed. The precipitate was filtered off, washed, dried, and weighed. The

filtrate was neutral; it was evaporated to dryness, ignited, and weighed, whence the weight of Na_2SO_4 in the filtrate was obtained. The numbers obtained were found to be in accordance with the equation

$$6Tl_2SO_4 + (Na_{12}V_8O_{26} + 12H_2O) = Tl_{12}V_8O_{26} + 6Na_2SO_4 + 12H_2O.$$

Since on adding thallium sulphate to a boiled solution of the hexvanadate we get a salt having the composition $Tl_{12}V_8O_{26}$, it was considered interesting to ascertain whether a corresponding silver vanadate is formed under similar circumstances. For this purpose, a portion of the sample of sodium vanadate used in the preparation of thallium octovanadate was dissolved in water, boiled, cooled, and a solution of silver nitrate added till no further precipitate was formed; the precipitate was washed, and dried at 105°.

On analysis it gave the following results:—

Wt. of precipitate taken = 0·2635 grm.

AgCl obtained = 0·2100 grm. = 0·15804 grm. Ag .... } Ag obtained = 0·01650 grm. Ag }	= 66·24 p. c. Ag	= 71·14 of Ag_2O
Wt. of V_2O_5 obtained = 0·074 grm.; p. c. of V	= 15·77	= 28·08 of V_2O_5
		99·22

These numbers correspond with the formula of silver pyrovanadate $Ag_4V_2O_7$, and not with the formula $Ag_{12}V_8O_{26}$.

	Found.	Calculated for $Ag_4V_2O_7$.	Calculated for $Ag_{12}V_8O_{26}$.
Ag	= 66·24	66·81	61·06
V	= 15·77	15·87	19·33
O	= —	17·32	19·61
		100·00	100·00

From this it is seen that silver does not form the abnormal pyrovanadate, which, under the same circumstances, is produced in the case of thallium.

γ-Thallium Vanadate or *Decavanadate*, $Tl_{12}V_{10}O_{31}$.—This salt was formed by adding a solution of thallium sulphate in excess to a boiled and cooled solution of fused sodium pyrovanadate containing a small excess of vanadic acid; but apparently, under the same circumstances, sometimes a precipitate was obtained approximating rather to the formula $Tl_{12}V_8O_{26}$.

The sodium pyrovanadate used contained 35·52 per cent. of vanadium, the calculated quantity for the formula being 33·46 per cent.

The precipitate at first formed was white, but on stirring and adding more of the thallium salt it became light yellow; it was washed with cold water by decantation, thrown on a filter, and dried at 100°. On heating a portion to 120°, it sustained no loss, neither did it give off any moisture on heating to fusion in a dry test-tube, and therefore contained no water. The filtrate from the precipitate was alkaline, and contained caustic soda.

The analyses of the salt thus obtained gave the following results:—

Preparation (1).

(*a.*) Wt. of salt taken = 0·2805 grm.

TlI obtained = 0·3210 grm.; p. c. Tl = 70·50 = 73·26 p. c. Tl_2O
V_2O_5 „ = 0·0740 grm.; „ V = 14·82 = 26·38 „ V_2O_5

99·64

(*b.*) Wt. of salt taken = 0·239 grm.

TlI obtained = 0·275 grm.; p. c. of Tl = 70·89 = 73·66 p. c. Tl_2O

(*c.*) Wt. of salt taken = 0·2175 grm.

V_2O_5 obtained = 0·0570 grm.; p. c. V = 14·73 = 26·21 p. c. V_2O_5
TlI „ = 0·2475 „ „ Tl = 70·13 = 72·88 „ Tl_2O

99·09

Preparation (2.)

(*d.*) Wt. of salt taken = 0·182 grm.

V_2O_5 obtained = 0·047 grm.; p. c. V = 14·51 = 25·83 p. c. V_2O_5

Preparation (3.)

(*e.*) Wt. of salt taken = 0·195 grm.

TlI obtained = 0·2235 grm.; p. c. Tl = 70·64

(*f.*) Wt. of salt taken = 0.2025 grm.

TlI obtained = 0·2345 grm.; p. c. Tl = 71·37

The mean of the above analyses is as follows, and corresponds to the formula $Tl_{12}V_{10}O_{31}$.

	Calculated.		Found.					Mean.	Difference.
			(*a.*)	(*b.*)	(*c.*)	(*f.*)	(*e.*)		
Tl_{12} =	2448	70·81	70·50	70·89	70·13	71·37	70·64	70·71	−0·10
						(*d.*)			
V_{10} =	513	14·84	14·82	—	14·73	14·51	—	14·69	−0·15
O_{31} =	496	14·35	—	—	—	—	—	—	—
	3457	100·00							

γ-Thallium vanadate or decavanadate corresponds to the second sodium phosphate ($Na_{12}V_{10}O_{31}$) of Henneberg and Fleitmann (*Ann.*

Chem. Pharm., lxv, 304, and Uelmann *Ann. Chem. Pharm.*, cxviii, 99). It is a light yellow powder of spec. grav. 7·86 at 17°. It is only slightly soluble in water, the numbers obtained being—

1 part of salt dissolves in	9372	parts of water at	11°
1 „ „ „	3366	„ „	100°

Thallium Metavanadate, $TlVO_3$, or *Dodecavanadate*, $Tl_{12}V_{12}O_{36}$.—Thallium metavanadate is prepared by fusing together one molecule of thallium carbonate with one molecule of V_2O_5:—

$$Tl_2CO_3 + V_2O_5 = 2TlVO_3 + CO_2.$$

The fusion was carried on over a Bunsen's burner; the thallium did not seem to have any tendency to volatilise during the operation, as in the case of the preparation of Tl_3VO_4 and $Tl_4V_2O_7$. The fused mass on cooling had a laminated, crystalline appearance, and was of a very dark colour. On powdering it became of a fine slate colour.

Two preparations of the salt were made in this way, and analysed as follows:—

Preparation (1).—(*a*). Wt. of salt taken = 0·129 grm.
TlI obtained = 0·1405 grm.; p.c. Tl = 67·12 = 69·75 p.c. Tl_2O
V_2O_5 „ = 0·0375 „ „ V = 16·33 = 29·09 „ V_2O_5

98·84

Preparation (2).—(*b*.) Wt. of salt taken = 0 272 grm.
TlI obtained = 0·296 grm.: p.c. Tl = 67 07 = 69·70 p. c. Tl_2O.

(*c*.) Wt. of salt taken = 0·2855 grm.
V_2O_5 obtained = 0·082 grm.; p. c. V = 16 14 = 28 72 p. c. V_2O_5.

The mean of the above analyses is represented as follows:—

	Calculated.		Found.			Mean.	Difference.
Tl =	204 0	67·25	67·12	67·07	—	67 09	−0 16
V =	51·3	16·89	16·33	—	16·14	16·24	−0·65
O_3 =	48·0	15·86	—	—	—	—	—

Thallium metavanadate, $Tl_{12}V_{12}O_{36}$, or $TlVO_3$, is a slate-coloured powder of specific gravity 6·019 at 17°; it is nearly insoluble in cold water, the numbers being—

1 part of salt dissolves in	11534	parts of water at	11°.
1 „ „	4756	„ „	100°.

Owing to the insolubility of sodium metavanadate in water, it was not practicable to use it in the preparation of thallium metavanadate; neither can the latter salt be obtained by adding a solution of thallium

sulphate to one of ammonium metavanadate, for in that case a red precipitate is formed, having the composition, $Tl_{12}V_{11}O_{41}$.

δ-Thallium Vanadate, or *Tetradecavanadate*, $Tl_{12}V_{14}O_{41}$.—This salt was obtained under the following circumstances:—

A. When a solution of thallium sulphate was added to ammonium metavanadate, a precipitate was obtained of the composition $Tl_{12}V_{14}O_{41}$. On analysis it always gave a lower percentage of thallium, and a higher one of vanadium than that required by the formula $TlVO_3$, the precipitate being of a red, or pinkish-red colour, while the ordinary metavanadate of thallium is slate-coloured.

B. The same salt is obtained by adding an excess of thallium sulphate to a solution of a sodium pyrovanadate, having the composition $Na_{12}V_{10}O_{31}$.

The following preparations were made by these methods:—

Preparation (1).—The ammonium metavanadate was dissolved in hot water, and when cold a solution of thallium sulphate added to excess. The precipitate at first formed was light yellow, very curdy, and rather gelatinous, settling after some time only; on adding more thallium sulphate, the precipitate became more curdy, settled sooner, and turned to a yellowish orange colour, which on stirring again became yellow. On standing, however, it changed to a greyish-white, crystalline powder, which after some days assumed a reddish tint.* It was then filtered, washed, and dried at 100°.

The analysis of the precipitate gave—

(*a*.) Wt. of salt taken = 0·165 grm.

TlI obtained	= 0.1695 grm.;	p. c. Tl = 63·46	= 65·94	p. c. Tl_2O
V_2O_5 ,,	= 0·0540 ,,	,, V = 18·38	= 32·72	,, V_2O_5
			98·66	

(*b*.) Wt. of salt taken = 0·2245 grm.

TlI obtained = 0·2325 grm. p.c. Tl = 63·82.

Preparation (2).—In this case a different sample of ammonium metavanadate was used; and an exact sufficiency of thallium sulphate added in the precipitation. The precipitate was at first curdy and yellow, but by degrees it became crystalline, and of a dirty white colour, and as more thallium sulphate was added, pinkish-red. The analyses gave:—

(*c*.) Wt. taken = 0·238 grm.

TlI obtained	= 0·2505 p. c.;	Tl = 64·86	= 67·40	p. c. Tl_2O
V_2O_5 ,,	= 0·0790 ,,	V = 18·65	= 33·19	,, V_2O_5
			100·59	

* The different changes of colour which take place during the formation of the thallium vanadates by precipitation, have not yet been fully investigated.

(*d.*) Wt. taken = 0·194 grm.
TlI obtained = 0·2015; p. c. Tl = 64·01 = 66·52 p. c. Tl_2O
V_2O_5 „ = 0·0660; „ V = 19·11 = 34·02 „ V_2O_5

100·54

Preparation (3).—In this case also a different sample of ammonium metavanadate was used.

The precipitate was at first yellow and curdy, then dirty-white, and lastly, on boiling, it became crystalline and pinkish-red.

(*e.*) Wt. taken = 0·237 grm.
TlI obtained = 0·2415; p. c. Tl = 62·80 = 65·26 p. c. Tl_2O
V_2O_5 „ = 0 0790; „ V = 18·73 = 33·33 „ V_2O_5

98·59

In each of the above preparations, there was only a barely perceptible trace of ammonia.

Preparation (4).—This sample was made according to method (B), by adding an excess of Tl_2SO_4 to a solution of a fused sodium pyrovanadate, having the composition $Na_{12}V_{10}O_{36}$ (obtained by fusing 6 molecules of Na_2CO_3 with 5 of V_2O_5). The precipitate formed was at first white, then yellow, and lastly red; it was washed, dried at 100°, and analysed.

(*f.*) Wt. taken = 0·2795 grm.
TlI obtained = 0·293 grm.; p. c. Tl = 64·60

The mean of the above analyses may be represented thus, and corresponds with the formula, $Tl_{12}V_{14}O_{41}$.

	Calculated.		Found.						Mean.	Difference.
			Prep. (1).		Prep. (2).		Prep. (3).	Prep. (4).		
			(*a.*)	(*b.*)	(*c.*)	(*d.*)	(*e*)	(*f*).		
Tl_{12} =	2448·0	64·04	63·46	63 82	64·86	64 01	62·80	64·60	63 92	−0·12
V_{14} =	718·2	18·79	18·38	—	18·65	19·11	18·73	—	18·72	−0·07
O_{41} =	656 0	17·17	—	—	—	—	—	—	—	—
	3822 2	100·00								

δ-Thallium vanadate, or tetradecavanate is almost insoluble in water. It is a crystalline powder of a pinkish-red colour.

The vanadates of thallium may be represented by the following formulæ, showing that they form a series, each member of which differs from the preceding one by 1 molecule of vanadium pentoxide.

Thallium tetravanadate	$Tl_{12}V_4O_{16}$, or $6Tl_2O\,2V_2O_5$ =	$4Tl_3VO_4$	Thallium orthovanadate
Thallium hexavanadate	$Tl_{12}V_6O_{21}$, or $6Tl_2O\,3V_2O_5$ =	$3Tl_4V_2O_7$	Thallium pyrovanadate
Thallium octavanadate	$Tl_{12}V_8O_{26}$, or $6Tl_2O\,4V_2O_5$ =	$2Tl_6V_4O_{13}$	Thallium β vanadate
Thallium decavanadate	$Tl_{12}V_{10}O_{31}$, or $6Tl_2O\,5V_2O_5$ =	$Tl_{12}V_{10}O_{31}$	Thallium γ-vanadate
Thallium dodecavanadate	$Tl_{12}V_{12}O_{36}$, or $6Tl_2O\,6V_2O_5$ =	$12TlVO_3$	Thallium metavanadate
Thallium tetradecavanadate	$Tl_{12}V_{14}O_{41}$, or $6Tl_2O\,7V_2O_5$ =	$Tl_{12}V_{14}O_{41}$	Thallium δ-vanadate

Since thallium so easily forms the abnormal vanadate $Tl_{12}V_8O_{26}$, it was considered interesting to prepare the corresponding sodium and silver compounds, and this was done as follows —

β-Sodium vanadate, or *Octovanadate*, $Na_{12}V_8O_{26} + 12H_2O$, is obtained by fusing together 6 molecules of sodium carbonate with 4 of vanadium pentoxide

$$6Na_2CO_3 + 4V_2O_5 = Na_{12}V_8O_{26} + 6CO_2$$

(1) The fused mass was dissolved in water and evaporated on a water-bath to a syrupy liquid, cooled, and allowed to crystallise out, which it did with great difficulty The crystals were dried between 90° and 100° The analysis gave—

Wt of salt taken = 0.3665 grm

V_2O_5 obtained = 0.1985 grm, p c V = 30.43 = 54.16 p c V_2O_5
NaCl „ = 0.1950 grm, „ Na = 20.92 = 28.19 „ Na_2O
0.5955 grm of salt lost on ignition,
0.105 grm of H_2O, p c of H_2O = 17.63

99.98

Another determination gave 16.81 p c H_2O, mean = 17.22 p c. H_2O

(2) Another preparation was made in the same way, and on analysis gave the following results, the percentage of water being less than in the former case —

Wt of substance taken = 0.2590 grm
Wt of V_2O_5 obtained = 0.1590 grm, p c V = 34.49 ... = 61.39 p c V_2O_5
Wt of NaCl obtained = 0.1535 grm, p c Na = 23.30 ... = 31.41 „ Na_2O
0.2555 grm of salt lost on ignition, 0.0165 grm = 6.46 „ H_2O

99.26

These results may be represented thus —

	Calculated.		Found.		Calculated.		Found.
			(1.)				(2.)
Na_{12} =	276·0	20·92	20·92	Na_{12} =	276·0	23·49	23·30
V_8 =	410·4	31·15	30·43	V_8 =	410·4	34·94	34·49
O_{26} =	416·0	31·55	—	O_{26} =	416·0	35·44	—
$12H_2O$ =	216·0	16·38	17·22	$4H_2O$ =	72·0	6·13	6·46
	1318·4	100·00			1174·4	100·00	

β-Sodium vanadate corresponds to the sodium phosphate of Henneberg and Fleitmann. It is a white, crystalline mass, which dissolves with great difficulty in a large quantity of cold water, being much less soluble than the ordinary pyrosalt, $Na_4V_2O_7$. The specific gravity of the preparation containing 4 molecules of water is 2·85 at 18°.

β-Silver vanadate, or Octovanadate, $Ag_{12}V_8O_{26}$, is prepared by dissolving sodium octovanadate in water, and adding a solution of silver nitrate, till no further precipitate is formed. The latter is of a dark yellow colour, very dense, and settles with difficulty. It is filtered off, washed, and dried at 110°.

The analyses gave:—

(*a.*) Wt. of salt taken = 0·212 grm.

$$\left.\begin{array}{l}\text{Wt. of AgCl} = 0·1255 \text{ grm.}\\ \quad ,, \quad \text{Ag} = 0·0335 \quad ,,\end{array}\right\} = 0·12795 \text{ grm. Ag.}$$

p. c. Ag = 60·35 .... = 64·82 p. c. Ag_2O

Wt. of V_2O_5 = 0·0735 grm.; p. c. V = 19·48 .... = 34·67 ,, V_2O_5

99·49

(*b.*) Wt. of salt taken = 0·2575 grm.

$$\left.\begin{array}{l}\text{AgCl obtained} = 0·1770 \text{ grm.}\\ \text{Ag} \quad ,, \quad = 0·0225 \quad ,,\end{array}\right\} = 0·155712 \text{ grm. Ag.}$$

p. c. Ag. = 60·46 .... = 64·94 p. c. Ag_2O

V_2O_5 obtained = 0·0905 grm.; p. c. V = 19·74.. = 35·14 ,, V_2O_5

100·08

The mean of the above analyses is as follows, corresponding with the formula, $Ag_{12}V_8O_{26}$:—

	Calculated.		Found.		Mean.	Difference.
			(*a.*)	(*b.*)		
Ag_{12} =	1296·0	61·06	60·35	60·46	60·41	−0·65
V_8 =	410·4	19·33	19·48	19·74	19·61	+0·28
O_{26} =	416·0	19·61	—	—	—	—
	2122·4	100·00				

The decomposition which takes place when this salt is prepared in the above manner was determined, and the numbers obtained were found to be in accordance with the equation—

$$12AgNO_3 + (Na_{12}V_8O_{26} + 12H_2O) = Ag_{12}V_8O_{26} + 12NaNO_3 + 12H_2O.$$

Silver octovanadate is a dark-yellow powder, of spec. grav. 5·67 at 18°; it is very slightly soluble in water, the numbers being

1 part of	salt dissolves in	21,414	parts of	water at	14°
1	„	„	13,617	„	„	100°

I conclude by thanking Dr. Roscoe for the kind and able advice which he has given me during the above research.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Experimental Researches on the Solar Spectrum. By N. Lockyer (Compt. rend., lxxv, 1816—1819).

The observation that the number and length of the lines in the spectra of metallic vapours depend upon the density of the absorbing or radiating vapour, and that only the longest lines remain visible when the vapours are rarefied, obtains additional importance by the author's discovery *that the inverted lines in the solar spectrum are without exception the longest lines observed in the spectrum of the vapour of each element.* The presence of zinc and aluminium in the sun had hitherto been extremely doubtful, as only very few lines of their spectra had been found inverted in the solar spectrum; this doubt we may now consider as removed, since the author has found that the lines corresponding to these elements in the solar spectrum are the longest lines of the spectra of their vapours.

R. S.

The Spectrum of Nitrogen. By A. Schuster (Pogg. Ann., cxlvii, 106—112).

The author has examined the so-called two spectra of nitrogen. His experiments seem to show that in reality pure nitrogen exhibits but one spectrum, viz., the line spectrum, that showing fluted bands being due to the presence of nitrogen oxides (probably in most part caused by nitric oxide).

Even very carefully-prepared nitrogen was found to contain traces of oxygen which, on the passage of the electric spark, combines to form nitrogen oxides. By placing a small piece of pure sodium in the vacuum-tube the last traces of oxygen were removed.

The true line spectrum of nitrogen invariably shows a bright green line, followed (towards the blue end of the spectrum) by a green band. The fluted spectrum shows shaded violet bands.

M. M. P. M.

The Spectra of Phosphoretted Hydrogen and Ammonia. By K. B. Hofmann (Pogg. Ann., cxlvii, 92—101).

The spectrum of phosphoretted hydrogen shows four green lines, lying between D and F (Fraunhofer).

The flame of this gas appears green, but if the gas be burned after having been for 2—3 hours in contact with rape-oil, the green colour is no longer seen. The green colour, according to the author, is not due to burning phosphorus, because phosphorus burned alone shows

no spectral lines; nor is it due to the burning of the gas phosphoretted hydrogen, because this gas when heated is split up. The chemical process going forward in the mantle of the flame is supposed by the author to produce beams of constant refrangibility, and the green colour to be due to these. The spectrum of ammonia was then examined; the lines are fully described and tabulated in the original paper. The flame is yellow, not green. This spectrum is not to be accounted for by the decomposition of ammonia and the burning of the nitrogen.

M. M. P. M.

The Spectrum of Chlorophyll. By J. CHAUTARD (Compt. rend., lxxv, 1836—8).

THE author gives a description of the absorption-bands produced by different thicknesses of an alcoholic solution of chlorophyll. He points out the persistency, under great dilution, of the band in the red portion of the spectrum. When the solution is treated with hydrochloric acid, the spectrum becomes very different, but the band in the red is still seen, even on great dilution. An alcoholic solution prepared from dried leaves gives a spectrum like that of the acidified solution from fresh leaves. The solution of fresh chlorophyll is also rapidly changed by exposure to sunshine, and more slowly by diffused light, so as to give a spectrum like that of acidified chlorophyll. Other colouring matters do not mask the presence of chlorophyll, and metallic salts, when first added and before precipitation takes place, do not affect its spectrum.

E. D.

Production of Light by Atomic Movements. By F. HOPPE-SEYLER (Pogg. Ann., cxlvii, 101—105).

MANY bodies emit light at ordinary temperatures. This fact forms the basis of a speculation by the author, in which he supposes that the atom of a substance may rotate without any appreciable movement of the molecules, and that the production of light may, in many instances, be due to such *atomic* movements.

These movements will depend upon the mass of the atoms and the chemical force binding them together. When these movements are so extensive as to cause a disruption of the molecule, a new substance is formed, accompanied by a greater emission of light. The tension of vapours and the change of volume upon increase of temperature are to be regarded as caused by *molecular* movements. The atomic movements causing emission of light-waves may be taken up by the molecules, and so we have absorption of light.

As the sphere of action between any two atoms must be limited, chemical decomposition will ensue as soon as these atoms pass out of this sphere; if their excursions exceed the distance between the middle points of the neighbouring molecules, a complete breaking-up of the molecule must ensue.

M. M. P. M.

Molecular Colours of the Metals. By W. STEIN (J. pr. Chem. [2], vi, 172—185).

THE author chiefly treats of the colour of gold and of "blue sulphur."

Gold in thin plates, or when precipitated from very dilute solutions (by action of sulphur dioxide in water) manifests dichröism, appearing indigo-blue by transmitted light, but reddish-yellow by reflected light. But if the particles of gold be very small (as when gold is precipitated from its solution by means of stannous chloride) the laws of interference come into play and the gold appears purple. Such gold the author calls molecular gold, and he thus distinguishes three modifications of gold (1) ordinary, (2) dichroitic, (3) molecular. Ruby-glass he regards as a solution of molecular gold in glass.

A somewhat similar phenomenon is exhibited in grinding transparent substances to fine powder; they then appear darker and non-transparent. The smaller the particles the darker their colour. The atoms of transparent bodies vibrate in unison with the white light vibrations of the atmosphere, but when the particles are reduced to small size, some of these vibrations are not taken up by them, but reflected: hence the colour now manifested by the substances; and, partly from the change into heat vibrations of the excess of those vibrations producing white light over those producing coloured light, partly from the interference of the different vibrations, heat is produced.

Similar phenomena are shown when sulphur trioxide acts on flowers of sulphur, a liquid being produced which appears blue by transmitted light. This the author regards as finely divided sulphur, held in suspension in sulphuric acid, the acid acting the part of a white screen held behind the particles of sulphur so as to transmit white light through them. M. M. P. M.

Researches on Elective Attraction. By E. J. MILLS (Phil. Mag. [4], xliv, 506).

THE law of chemical attraction which forms the subject of this memoir, was deduced from the results of a series of experiments which had their origin in an attempt to prepare nitryl chloride by the action of phosphorus oxychloride upon certain nitrates. Although the reaction was unsuccessful as a source of the above-mentioned chloride, it was obvious that the decomposition proceeded with a certain uniformity, and upon analysis of the residual products, it was observed that in any series of operations with the same nitrate, the ratio between the weights of chlorine retained and phosphoric oxide produced were sensibly constant. This ratio, multiplied by 4·06 or $\frac{Cl}{P_2O_5}$ is designated by the symbol α.

The experiments were thus conducted. A weighed quantity of pure anhydrous nitrate was placed in a suitably arranged reaction-tube, a proportion of phosphorus oxychloride (free from hydrochloric acid and non-fuming) added, and heat gradually applied until the action reached a maximum; a current of *absolutely* dry air passing slowly through

the apparatus during the whole operation. When no more coloured gases were expelled, it was judged that the reaction was completed; the excess of oxychloride was then distilled away, and the residue after weighing was dissolved in water and analysed.

The nitrates of silver, lead, thallium, potassium, sodium, lithium, cæsium, and rubidium were submitted to experiment. Barium nitrate was not attacked by phosphorus oxychloride. The accompanying table is selected as an example of the manner in which the results are returned:—

	I.	II.	III.
Silver nitrate employed	2·1746	1·0519	2·7633
Residue obtained	2·1800	1·0589	2·7345
Temperature	121°	120°	120°
Composition of the residue, viz.,			
Silver nitrate	40·77	25·96	57·87
Silver chloride	49 77	61·91	36·44
Phosphoric oxide	9·47	12·93	6·60
	100·01	100·80	100·91
Hence the values of a are respectively	5·21	4·74	5·47

It must be observed that the residual nitrate is calculated, not by difference, but from the original nitrate on the basis of the chloride found. In the case of the potassium salt, the amount of nitrate obtained by calculation did not even remotely approximate to the undetermined difference, and a determination of the unattacked nitrate by Harcourt's process was also unsuccessful.*

The analysis of the lithium residues was attended with several inconveniences, inasmuch as the mass in the tube became vesicular, and finally interrupted the passage of air; from this circumstance, the oxychloride never wholly distilled away, and had, consequently, to be determined by another operation. In the case of thallium nitrate, the dichloride, and not the sparingly soluble thallious chloride, was the result of the reaction.

Mean values of a—

Potassium nitrate.	Sodium nitrate.	Thallium nitrate.	Silver nitrate.
2·001	1·70	4·38	5·48
Lead nitrate.	**Lithium nitrate.**	**Cæsium nitrate.**	**Rubidium nitrate.**
5·17	1·61	2·21	2·38

* The author finds that in Harcourt's process, if the potassium nitrate be mixed with a small proportion of potassium phosphate, the whole of the nitrate is not decomposed in the ordinary manner, and that the apparent yield requires to be multiplied by the number 1·0689. When the phosphate is absent, a normal number is obtained.

The numbers to which α corresponds are ratios and not absolute quantities; they represent the potential energy or dynamical use which can be made of a nitrate; they are obtained under a law of chemical action, and are in themselves independent of any adventitious circumstances of manipulation. When one nitrate surpasses another in the power of fixing chlorine per unit of phosphoric oxide, that is an index of superior chemical activity, or to name the ultimate cause, attraction; and since this attractive effect can be estimated for several nitrates in a series, α becomes the coefficient of elective attraction of the nitrates.

If α be divided by the molecular weights of the several nitrates, calculated to an uniform weight of oxynitryl (NO_3), the following numbers are obtained:—

	α.	Σ.	Q.
Thallious nitrate	8·76	265·3	30·29
Silver	5·48	169·94	31·01
Lead	5·17	165·56	32·02
Rubidium	2·38	147·40	61·93
Cæsium	2·21	195·01	88·24
Potassium	1·99	101·14	50·82
Sodium	1·70	85·05	50·03
Lithium	1·61	69·00	42·86

It will be seen that the elective coefficient is directly proportional to the symbolic (molecular) value, and that, with one exception, α and Σ increase and diminish in regular order; the quotients Q, therefore, represent the weights of nitrates which correspond to the *unit* of elective attraction, and are strictly equivalent quantities. If these numbers be considered as an incomplete arithmetical series of which the most probable value of the first term is 6·258, some interesting results are observable. The mean product of symbolic value into the specific heat is 6·246, and the identity of this number with the foregoing term is unmistakeable. If s = specific heat, $\Sigma s = n\ 6{\cdot}25$, n being integral. But $Q = m\ 6{\cdot}25$, or since the results of experiment show that $m > n$; let $m = x\ n$; then by combining these two equations, we obtain $\alpha = \frac{1}{x s}$ as the expression of the elective attraction in terms of the specific heat.

Again, comparing any two coefficients (α and α') we have $\alpha : \alpha' :: \frac{1}{xs} : \frac{1}{x's'}$; but in several instances $x = x'$, as is obvious from the foregoing table. Then $\frac{\alpha}{\alpha'} = \frac{s'}{s}$.

The following instances may be adduced in verification of the latter case:—

$$\frac{\alpha\ \text{(potassium nitrate)}}{\alpha\ \text{(sodium nitrate)}} = 1{\cdot}17 \text{ by the method of ratios.}$$

$$= \frac{{\cdot}2782}{{\cdot}2388} = 1{\cdot}17 \text{ by specific heat.}$$

$$\frac{\alpha \text{ (thallious nitrate)}}{\alpha \text{ (silver nitrate)}} = 1\cdot59 \text{ by the method of ratios.}$$

$$= \frac{\cdot1433}{\cdot0942} = 1\cdot53 \text{ by specific heat.}$$

The memoir concludes by drawing attention to some examples from ordinary chemical experience, which prove that the intensity of elective attraction is in many cases, and probably in many more, proportional to symbolic value.

J. W.

Fractional Distillation. By J. A. Wanklyn (Phil. Mag [4], xlv, 129).

If quantities a and b of two volatile liquids be mixed together, and v and v' be the respective coefficients of volatility of the two liquids, the quantities of the two substances contained in a small quantity of distillate $= \delta$, will be respectively—

$$\frac{a\,v\,\delta}{a\,v + b\,v'}, \text{ and } \frac{b\,v'\,\delta}{a\,v + b\,v'}.$$

The heating being thus continued, the quantities of the two substances contained in a new portion $= \delta$ of distillate, are given by the same formulæ, where the quantities—

$$a - \frac{a\,v\,\delta}{a\,v + b\,v'}, \text{ and } b - \frac{b\,v'\,\delta}{a\,v + b\,v'},$$

are respectively substituted for a and b in the original formulæ: if then $v < v'$, the quantity of the first liquid in the successive quantities (each $= d$) of distillate, must progressively increase; whilst if $v > v'$, these quantities must successively diminish, the alterations in composition being the more rapid the greater the difference between v and v'.

In the values v and v' the latent heats of evaporation of the liquids, their vapour-densities, and the tensions of their vapours at the particular boiling point of the mixture, are concerned; and possibly, also, adhesion between the liquids; the author considers (on grounds not et published) that the formula—

$$v = td^2$$

(where $t =$ the tension of the vapour and $d =$ the vapour-density) expresses the value of the coefficient of volatility in most cases.

In four experiments on the distillation of weak ammonia solutions, the following results were obtained:—50 c.cs. of liquid were distilled off from a kilogram of each of four solutions, and the ammonia contained in the distillate titrated.

Ammonia per litre of original fluid.	Ammonia in 50 c cs. of distillate.
1000 milligrams.	480 milligrams.
1 "	0·5 "
0·5 "	0·235 "
0·2 "	0·095 "

The strength of the distillate is therefore, with fair approximation, proportional to the original strength, and the same result holds if other equal quantities (say 100 c.cs.) be distilled off in each case. Taking the coefficient of volatility of water as unity, the distillate is 9 6 times as strong as the original fluid, and hence the coefficient of volatility of ammonia would be 9·6 were so small a quantity volatilised as not sensibly to alter the composition of the residual liquor. As, however, this becomes weakened from 1000 milligrams per litre to 547 (1000 − 480 per 950 c.cs), the coefficient of volatility of ammonia is greater than 9·6: the strength of the first drop of the 50 ccs. of distillate being to that of the last drop of the same in the ratio 1000 to 547, the true value of the coefficient of volatility must be between 13 and 14.

C. R. A. W.

Investigations on Diosmose. By J. Baranetzky (Pogg. Ann., cxlvii, 195—245).

The author describes at length the results of earlier experimenters. His own apparatus is so arranged that the membrane is vertical, and the pressure on both sides kept equal during diffusion. He tried various membranes—pigs' bladder purified with alcohol; parchment paper; collodion films; and an artificial cellulose membrane prepared by denitrating a collodion film with a cold solution of ferrous chloride. The artificial cellulose retains the glassy, structureless character of a collodion film, but reacts as cellulose with a solution of iodine in potassium iodide, and with polarised light; it always contains, however, a little unaltered pyroxylin. The collodion films were laid in water before they were dry: if this is not done they are impervious to water. The diosmotic properties of the four membranes for weak solutions of calcium and sodium chloride were compared, a 30 per cent. solution of sugar being used as the second fluid. The amount of salt which diffused for the same increase in volume of the sugar solution was practically the same in the case of bladder and parchment paper, rather less with the cellulose, and much more with the pyroxylin membrane. The thinner the pyroxylin membrane, the greater was the proportion of salt to water that it transmitted. The author points out that all this agrees with Brücke's theory, that the endosmose of a fluid depends on the attraction of the membrane for that fluid. The first three membranes swell up readily in water, the pyroxylin does not. When the strength of the saline solution was varied, it appeared that the alteration in the rate of diffusion was in the same proportion for every membrane. The same membrane appears to have a different attraction for various salts. The author allowed dilute solutions (1 and 2 per cent.) of calcium chloride, sodium chloride, sodium nitrate, sodium sulphate, and magnesium sulphate to diffuse through parchment paper into pure water, the experiments being continued for the times given by Graham as sufficient to effect the diffusion of the same weight of each salt in the absence of any membrane Under these conditions equal weights of the first three salts diffused, but a smaller quantity of the sodium sulphate, and a still smaller quantity of the magnesium sulphate: in the latter cases the membrane had plainly a retarding influence. En-

dosmose of water ceases when the salt-solution on each side of the membrane is of nearly the same strength. With very weak solutions of magnesium sulphate endosmose of water ceased with the cellulose membrane when the stronger solution contained only ·15 per cent. of salt more than the weaker; it ceased with parchment-paper with an excess of ·5 per cent.; with pyroxylin at an excess of 1·0 per cent. The attraction of the membrane for water clearly influences this result.

Dutrochet attributed a high endosmotic attraction to colloïds; the author shows that colloids when purified by dialysis exert very little attraction. Solutions of albumin and gum arabic so purified, may be concentrated, the former to 10 per cent., the latter to nearly that extent, without gaining in volume when separated from pure water by bladder, parchment-paper, or cellulose membrane. Tannin acts rather more powerfully than gum arabic. If ordinary gum arabic be taken, or a little saline matter be added to the purified gum, the endosmotic attraction is decidedly greater. A pyroxylin membrane behaves very differently towards colloids; a solution of gum which produces no endosmose with the other three membranes occasions a large endosmose of water with pyroxylin. The thinner the pyroxylin membrane, the greater the endosmose. The attraction of the membrane for water appears, in the case of colloids, to oppose the endosmose. When colloïds are separated by membrane from a very weak saline solution, the endosmose is far less than with pure water; this holds good for all four membranes.

With regard to the processes of the living plant, the author believes that protoplasm rather than cellulose plays the principal part as a diosmosing membrane.

The author does not give the complete data of his experiments.

R. W.

Action of Solid Bodies upon Supersaturated Solutions.

By C. F. Henrici (Pogg. Ann., cxlvii, 555—569).

When solid bodies are brought in contact with liquids which contain gases in solution, three cases may be distinguished: (1) The attraction between liquid and gas is predominant; in this case no essential change will be effected by the immersion of a solid body; (2) The attraction between the solid and the gas predominates; then the gas is condensed on the surface, but not eliminated in the form of bubbles; (3) The attraction between the solid and the liquid predominates; then the liquid is condensed on the solid surface, and the gas is eliminated.

The author's experiments refer to the third case. Clean surfaces prepared by rubbing pieces of metal, bone, or glass between leather strewed over with pumice-stone powder, were immersed in ordinary well-water or in water supersaturated with carbonic acid by addition of a small quantity of Seidlitz powder. In both cases the surfaces became completely covered with gas-bubbles. Surfaces which have been heated in a flame do not exhibit this phenomenon, probably because they become covered with a carbonaceous film, which prevents the formation of bubbles by absorbing the gas which is eliminated by the

condensation of the liquid. The existence of some film on surfaces which have been in a flame may be inferred from a certain very slight resistance which is felt when they are drawn through a soft linen cloth.

Liquids containing very little gas exhibit the above phenomena in a very distinct manner on being placed in a glass vessel upon a heated plate, evidently because the affinity between gas and liquid is weakened by increase of temperature.

The experiments with leaves which are covered with extremely fine hairs prove that projecting points or a very slight roughness favour the separation of the bubbles. A bubble once being formed, air from the surrounding liquid enters into it in the same manner as it passes from the surface of the liquid into the atmosphere. The bubbles are not in contact with the surface; they do not unite with each other, and they do not attain the same size on glass as on metals. Gas-bubbles seem to be formed whatever may be the cause of the condensation of the liquid; by bringing a drop of some saline solution, or of potash upon the surface of water, bubbles are evolved as the saline liquid sinks to the bottom.

The sudden appearance of bubbles on striking a glass of champagne is probably also due to a temporary condensation of the liquid.

Some experiments are mentioned referring to the case in which the affinity between the solid body and the absorbed gas is greater than that between the gas and the liquid. Previously ignited pieces and powder of charcoal and of graphite were immersed in water richly charged with carbonic acid; but no gas-bubbles were observed, because the gas, instead of being eliminated, was condensed and absorbed on the solid surface.

When silver or platinum wire was immersed in strong ammonia-solution, increase of temperature was necessary for the separation of gas-bubbles. This experiment illustrates the first case in which the affinity between gas and liquid is predominant.

No gas-bubbles were observed on the surface of fats and oils in contact with water which was saturated with carbonic acid.

R. S.

On the Action of Electricity on Gases. By Sir B. C. BRODIE (Proc. Roy. Soc., xx, 472; Phil. Mag. [4], xliv, 470).—An abstract of a paper in the Philosophical Transactions, which does not admit of further condensation. The paper is intended to be the first of three communications as to the action of electricity on gases, and is devoted to the consideration of the action of electricity on oxygen gas, as estimated by the changes thus effected in its chemical properties.

Electromotive Force of very thin Gas-strata. By F. KOHLRAUSCH (Pogg. Ann., cxlviii, 143).

On the best Arrangement of Wheatstone's Bridge for Measuring a given Resistance with a given Galvanometer and Battery. (Phil. Mag. [4], xlv, 114).

Heat Spectrum of Solar Light and of the Lime Light. By L. LAMANSKY (Pogg. Ann. cxlvi, 200).

Heat-conducting Power of Iron and German Silver. By H. WEBER (Pogg. Ann, cxlvi, 257).

Description of a Pressure-regulator. By LOTHAR MEYER (Ann. Ch. Pharm., clxv, 303).

The Physometer—a new Instrument for Determining the Variable Volumes of Air and other Bodies. By P. HARTING (Pogg. Ann., cxlviii, 126).

Inorganic Chemistry.

Action of Sulphurous Acid upon recently Precipitated Insoluble Sulphides. By A. GUEROUT (Compt. rend., lxxv, 1276—1277).

LANGLOIS having shown that sulphurous acid converts soluble sulphides into thiosulphates, experiments were made to ascertain whether recently precipitated insoluble sulphides were thus acted on. The sulphides of copper, silver, gold, platinum and mercury, are not attacked by sulphurous acid. The sulphides of manganese, zinc, iron, cobalt, nickel, cadmium, bismuth, tin, arsenic and antimony, when freshly precipitated, are converted by it into thiosulphates, with deposition of sulphur and disengagement of quantities of hydrosulphuric acid varying for each metal.

The first three of these sulphides become readily soluble in the sulphurous acid solution, the remainder slightly soluble. Lead sulphide is only very partially converted into thiosulphate, the remaining and larger portion becoming sulphite, with deposition of sulphur and evolution of much hydrosulphuric acid. No sulphuric acid is formed in any of the above cases if air be excluded. The following equations, proposed by Langlois, express the reactions which take place:—

$$(1.)\ MS + SO_2 + H_2O = MSO_3 + H_2S$$
$$(2.)\ 2H_2S + SO_2 = 2H_2O + 3S$$
$$(3.)\ MSO_3 + S = MS_2O_3.$$

The correctness of this mode of expressing the changes that take place is proved thus:—when sulphurous acid is dropped slowly into water containing manganese sulphide in suspension, with constant agitation, the sulphurous acid is in contact with a large excess of sulphide; some of the hydrosulphuric acid formed ought, therefore, to escape the action of the sulphurous acid, and, in consequence, some of the sulphite would not be converted into thiosulphate. And this is what actually takes place: much more hydrosulphuric acid is evolved, and a much larger quantity of sulphite is formed under these condi-

tions, than when the sulphurous acid is at once added in excess. Again, the small amount of thiosulphate formed in the case of lead sulphide is evidently due to the insolubility of lead sulphite, which renders it less liable to the action of the nascent sulphur.

B. J. G.

Liquid Carbon Dioxide. By L. CAILLETET (Compt. rend., lxxv, 1271—1274).

THILORIER, who first described the properties of liquid carbon dioxide (*Ann. Chim, Phys.*, lx, 427), did not state under what conditions his experiments were made.* The author's apparatus (see *Compt. rend.*, lxx, 1131) consists of a steel "laboratory-tube" containing mercury, and communicating, by means of a copper tube, with a cylinder of steel containing water. On the surface of the water presses a piston, the rod of which is a screw working in a screw-box. This box is fitted to the axle of a wheel, by turning which a pressure of 900 atmospheres can be communicated to the mercury in the laboratory-tube. The dry gas is collected in a sort of large thermometer having its reservoir open at the bottom, and its stem made of thick glass. This instrument is plunged, with the open part downwards, into the laboratory-tube, leaving the stem alone projecting above. On applying pressure, the mercury will rise in the glass stem till the gas is liquefied. The observer must be protected by a thick plate-glass screen. Thus obtained, liquid carbon dioxide is colourless and mobile. It is a non-conductor of electricity: when the ends of the wires of a powerful induction-coil are brought near each other in this liquid, a brilliant white light is produced, unaccompanied by any deposit of carbon. The coefficient of compressibility could not be determined with accuracy owing to the presence of a small quantity of uncondensed gas.

The analogy between carbon dioxide and water, led the author to submit various substances to the action of the liquefied gas by passing them up into the glass tube before condensing. The following are insoluble in liquid carbon dioxide: sodium chloride, sodium sulphate, calcium chloride, calcium carbonate, sulphur, phosphorus, stearin and paraffin. Neutral sodium carbonate is converted into acid sodium carbonate, which is insoluble in the liquid. Iodine dissolves sparingly, giving the tint produced by 5 milligrams of iodine in 10 c.c. of carbon sulphide. The liquid fats are slightly soluble in liquid carbon dioxide; tallow is bleached by the abstraction of its liquid fats. Petroleum oil dissolves 5 or 6 times its volume. It appears to be miscible with ether in all proportions. Carbon sulphide takes up a small proportion only. Liquid carbon dioxide is not reduced by sodium.

B. J. G.

Carbon Oxysulphide. By F. SOLOMON (J. pr. Chem. [2], v, 476—480).

THE author has made a series of experiments on the carbon oxysulphide prepared from potassium sulphocyanate and sulphuric acid, and on the

* The author does not appear to be acquainted with the experiments of Mr. Gore (*Chem. Soc. Journal*, xv, 163).—ED.

carbon oxysulphide produced by the direct union of carbonic oxide and sulphur, by converting them into potassium monosulphocarbonate by passing the gas into alcoholic potash. These two salts were compared with that obtained by Debus, by the decomposition of ethylic xanthate by alcoholic potash, which must be considered to have the formula, $CS\left\{\begin{matrix}OC_2H_5\\OK\end{matrix}\right.$. These three substances were found to be identical, and therefore Kolbe's suggestion that there are two oxysulphides of carbon, (CS)O and (CO)S, is not confirmed. The best method for procuring oxysulphide of carbon is to pass carbonic oxide and sulphur vapour through a red-hot glass tube, and absorb the gas by alcoholic potash, from which it can be liberated in the pure state by the action of hydrochloric acid.

A. P.

Some Reactions of the Chlorides of Boron and of Silicon. By L. TROOST and P. HAUTEFEUILLE (Compt. rend., lxxv, 1819—1821).

WHEN the vapour of chloride of boron is passed through a porcelain tube, either glazed or unglazed, the substance of the tube is rapidly attacked at a bright red heat. The chloride of boron is partially decomposed, chloride of silicon and chloride of aluminium are volatilised, while borate of aluminium remains behind. With a glazed tube, a certain quantity of the double chloride of aluminium and potassium is also formed. This result induced the authors to submit to the vapour of the chloride successively, pure alumina, silica, zirconia, and titanic acid contained in a platinum tube. In every instance a similar result was obtained, save that in the case of the three latter substances, the residue consisted of boric anhydride.

The vapour of chloride of silicon, on the contrary, has no action on porcelain, or on its felspathic glaze, even at a temperature at which the porcelain began to soften; it does not attack silicate of aluminium, but if it be passed over pure alumina contained in a platinum or porcelain tube, decomposition of the chloride results, and chloride of aluminium is volatilised.

The vapour of chloride of silicon also attacks zirconia, but is without action upon titanic acid.

J. W.

Hydrated Silicic Acid. By J. GOTTLIEB (J. pr. Chem. [2], vi, 185—196).

THE author prepared silicic acid by decomposition of silicon fluoride. After drying over sulphuric acid for about 160 days, the percentage of water was 6·13.

After drying at 100° for 3—4 days in a peculiar apparatus (fully described in the original paper), the percentage of water was 4·47, agreeing almost perfectly with the percentage obtained from silicic acid dried in an air-bath at 130°—140°.

The amount of water in the first-named hydrate, viz., 6·13 per cent., points to the formula, $H_4Si_9O_{20}$. The hydrated acid dried at 100° nearly agrees with the formula $H_4Si_{13}O_{28}$.

Referring to Maschke's researches, the author points out that silicic acid precipitated from very dilute solution, gives up water, on drying, more easily than that obtained by decomposing silicon fluoride.

M. M. P. M.

On some Compounds in which Phosphorus appears to exist in an Allotropic State. By ARM. GAUTIER (Compt. rend., lxxv, 49—52; lxxvi, 173—176).

I. PHOSPHORUS trichloride heated with crystallisable phosphorous acid to 170° in a sealed tube, furnishes a reddish-brown mass, the colour of which is due to the deposition of amorphous phosphorus, according to the following equation:—

$$3PCl_3 + 7PH_3O_3 = 4P + 3P_2H_4O_7 + 9HCl.$$

If, however, the temperature is not allowed to rise beyond 79°—80°, hydrochloric and pyrophosphoric acids are still formed, but a bright yellow substance gradually separates, which may be purified by distilling off the excess of phosphorous chloride, and washing the residue with ice-cold water. The yellow powder thus obtained, dried first *in vacuo*, then at 140° in a current of carbonic anhydride, has been submitted three times to analysis, and has given closely concordant results, leading to the formula, P_4HO.

If the reaction is allowed to take place at a temperature above 80°, the product is contaminated with amorphous phosphorus.

The compound P_4HO is yellow, amorphous, unchangeable in dry air, but undergoes oxidation in moist air. It is insoluble in all the solvents employed, water, alcohol, ether, benzene, chloroform, essence of turpentine, even at 150°, glycerin, acetic acid, phosphorous acid, and phosphorous or antimonious chloride. It is a very stable body, and may be heated to 250° in dry carbonic anhydride, without losing weight. Towards 265° it evolves phosphine, and sets free a little common phosphorus, but it is only at 350°—360°, that the phosphorus volatilises freely, leaving an oxidised residue which attacks the glass.

The compound is not affected by dilute acids, but ordinary nitric acid attacks it so violently as to produce a bright light. Water at 170° decomposes it easily, with evolution of pure phosphine—

$$2P_4HO + 11H_2O = 5PH_3O_2 + PH_3O_3 + 2PH_3.$$

Very dilute alkaline solutions act upon the body P_4HO, causing the disengagement of a mixture of phosphine and hydrogen, and furnishing solutions of phosphate and hypophosphite, together with an insoluble brown substance, which when exposed wet to the air, seems to reproduce the original compound.

Ammonia unites directly with P_4HO, producing a compound from which ammonia is withdrawn by the action of heat or of hydrochloric acid.

The author believes that the body here described is identical with the yellow substance which was obtained by Le Verrier, in 1837, by exposing to the air phosphorus immersed in phosphorus trichloride, and

was regarded by him as an oxide having the formula P_4O. The difference between this formula and that of the new substance is represented by a single atom of hydrogen, of the existence of which, however, in the latter the author has assured himself by special experiments.

II. The yellow powder often produced in the decomposition of phosphorus di-iodide by water is similar in some respects to the preceding. It appears to be invariably formed when the iodide is decomposed by a large quantity of water.

Analysis leads to the formula P_5H_3O, and the formation of the body may be explained by the following equation :—

$$12PI_3 + 24H_2O = P_5H_3O + 3PH_3O_4 + 3PH_3O_3 + PH_3O_2 + 24HI.$$

During the reaction there is disengaged a quantity of phosphine, resulting from the further action of water upon the yellow body:

$$P_5H_3O + 6H_2O = PH_3O_3 + 2PH_3O_2 + 2PH_3.$$

When the substance P_5H_3O is heated gradually to 275° in a current of carbonic anhydride, it evolves phosphine, and leaves a residue which undergoes no further decomposition till the temperature is raised to 350°, and to which analysis assigns the formula, $P_{13}H_3O_3$:

$$3P_5H_3O = 2PH_3 + P_{13}H_3O_3.$$

The author believes this body to be a definite chemical compound, but his investigation of the subject is not yet complete.

The compound P_5H_3O forms an unstable compound with ammonia.

W. A. T.

Neutral Calcium Phosphate. By E. Reichardt (Zeitschr. anal. Chem., xi, 275—277).

It was found that when a dilute solution of calcium chloride is precipitated by a small quantity of sodium phosphate, a precipitate which dissolves on agitation is produced, the redissolution being apparently due to the presence of carbonic acid in the water. A further addition of sodium phosphate reproduces the precipitate, and it may be again dissolved by passing a current of carbonic acid through the mixture. After some repetitions of this operation, the liquid deposits shining crystals, which were found to be identical with Boedeker's tetra-hydrated dicalcic orthophosphate, $Ca_2H_2P_2O_8.4H_2O$.

When this compound is boiled with water, it is partially decomposed; the portion remaining undissolved gave results agreeing with the formula, $Ca_3P_2O_8 + Ca_2H_2P_2O_8 + 3H_2O$, and the solution yielded, on evaporation, a residue which, after ignition, gave numbers corresponding with the formula $4CaO.3P_2O_5$. This substance dissolves in 3325·5 parts of water.

T. B.

Constituents of Bone Phosphates. By CARL AEBY (J. pr. Chem. [2], vi, 169—171.)

FRESH bones contain more carbon dioxide than a corresponding weight of burnt bones.

The author has determined also the constitution of fossil bones. It would appear that carbon dioxide enters into the composition of bone phosphates, not only as forming calcium carbonate mechanically mixed with the phosphates of calcium, but also as a constant constituent *per se*. The carbon dioxide which exists in this form may be driven off, together with water of crystallisation, by heating to 450°, and cannot be restored by treatment with ammonium carbonate. After ignition and addition of ammonium carbonate, the weight and composition of the bone phosphates are the same as after six hours' heating to 450°. The author's analyses seem to show that bone phosphates possess a much more complex structure than is usually assigned to them.

M. M. P. M.

The Nature of the Alkaline Chromates. By F. MOHR (Zeitschr. anal. Chem., xi, 278).

THE author has already pointed out that potassium bichromate is in reality a neutral salt, as it does not decompose potassium iodide. The addition of acetic acid to a solution containing potassium iodide and potassium bichromate, causes the gradual liberation of iodine.

The author finds that 1 gram of potassium chromate dissolved in 50 c.c. of water absorbs ·183 gram of carbonic acid, the liquid assuming the colour of potassium bichromate; it does not, however, acquire the property of liberating iodine from a solution of potassium iodide.

In order to determine the basicity of potassium chromate, 2 grams were distilled with ammonium chloride. The first distillate was found to contain 0·1428 gram of ammonia, and the residue in the retort exhibited the red colour of potassium bichromate. When the liquid was distilled to dryness, a further quantity of ammonia was obtained, making in all ·187 gram. Free chromic acid expels ammonia from its salts.

Potassium bichromate being a neutral salt, does not require a half atom of water like the corresponding potassium bisulphate.

T. B.

On Ammonium Molybdate. By L. KAEMMERER (J. pr. Chem. [2], vi, 358—360).

SOME ammonium molybdate residues from phosphoric acid determinations, on standing for six months, deposited a salt which was found to have the composition represented by the formula $(NH_4)_2O.3MoO_3 + H_2O$. The same salt was previously obtained by Berlin (*J. pr. Chem.*, xlix, 444).

J. R.

Preparation of Pure Manganous Oxide. By F. KESSLER (Zeitschr. Anal. Chem., xi, 270).

A SOLUTION of potassium permanganate saturated at 60°, filtered through paper free from lime, is added to a saturated oxalic acid solution, and the liquid is decomposed with acetic acid and boiled. The precipitate is repeatedly washed with water by subsidence and decantation, dried in a platinum basin, ignited and reduced in a stream of pure dry hydrogen.

Thus prepared, manganous oxide possesses a light green colour, the solution in dilute hydrochloric acid being slightly brown.

·9456 grm. converted into sulphate gave 2·0136 instead of 2·0111 grm., the atomic weight of manganese being = 55.

M. M. P. M.

Preparation of Anhydrous Cuprous Oxide of a fine Vermilion Colour. By R. BÖTTGER (Chem. Centr., 1872, 755).

TWO parts of potassium hydrate are dissolved in 16 parts of water in a porcelain basin, 1 pt. of starch sugar is added, and then 1 pt. of cupric tartrate; the mixture is heated to about 60° till it assumes a bright and deep red colour, and then immediately poured into a considerable quantity of well water previously de-äerated by boiling.

H. W.

Atomic Weight of Thallium. By W. CROOKES (Proc. Roy. Soc., xx, 475).

THE author has redetermined the atomic weight of this metal by ascertaining the quantity of thallious nitrate, $TlNO_3$, obtained by treating a known weight of thallium with nitric acid in a bulb-apparatus exhausted of air, elaborate precautions being taken to prevent the access of atmospheric oxygen, and to eliminate any sources of error arising from possible inaccuracy in the weights employed, &c., &c.

The mean of ten closely agreeing determinations gave—

$$Tl = 203·642.$$

H. W.

Mineralogical Chemistry.

A New Silico-aluminate of Manganese, containing Vanadium, from Salm-Château, Belgium. By F. PISANI (Compt. rend., lxxv, 1542).

THIS mineral occurs in the form of small, tabular, crystalline masses, embedded in quartz. It has a vitreous or resinous lustre, with a slightly nacreous appearance upon the faces of cleavage, and a resinous fracture. Translucent in thin layers, of a yellow or yellowish brown colour, and very brittle. Hardness = 7. Specific gravity = 3·577.

The crystals are doubly refractive, the two optic axes lying in a plane perpendicular to the plane of cleavage. The dispersion is very considerable, and the general optical properties of the mineral are such as to lead to the conclusion that the crystalline form is that of an oblique rhombic prism. It melts very easily before the blowpipe, but is not attacked by acids. When heated with phosphoric acid, it gives an almost colourless liquid, which becomes violet only after the addition of nitric acid.

Analysis.

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	CuO.	V_2O_5.	H_2O.	
28·70	28·36	2·94	26·40	4·30	4·32	1·30	1·80	0.98	= 99·10

The oxygen ratio is $SiO_2 = 5$. $R_2O_3 = 5$. $RO = 3$.

Lasaulx, who simultaneously examined this mineral, suggested for it the name *mangandisthene*. The author, however, objects strongly to this appellation, pointing out that the crystallographic and optical characters are altogether different from those of a disthene, and that it contains protoxide and not sesquioxide of manganese. He proposes to name it *dewalquite*.

J. W.

A New Silver-amalgam. By F. PISANI (Compt. rend., lxxv, 1274—1275).

A SAMPLE of native silver of a dead-white colour, from the Konsberg mine in Norway, occurring in large cubes, the angles of which were often deeply truncated, gave on analysis, silver = 95·26, mercury = 4·74. Another sample from the same place, the crystals of which were smaller and not so well defined, of a brass-yellow colour from iridescence, gave silver = 94·94, mercury = 5·06. The mean of these two results corresponds with the formula, $Ag_{36}Hg$. If the above composition be not accidental, but be confirmed by the discovery of other specimens, it is proposed to call the mineral *Kongsbergite*. The author inclines, however, to the opinion that amalgams are more of the nature of alloys than of binary compounds, and that, therefore, their constituents may be in any proportion to each other. The same mine from which these specimens were obtained furnished a sample of arquerite.

B. J. G.

Two Pseudomorphoses. By AMUND HELLAND (Pogg. Ann., cxlv, 480—484).

A CASE of pseudomorphosis of garnet into mica has been found in the mica crystals occurring in a vein of pegmatite at Roestoel, near Arendal. As in another part of the same vein a great number of unchanged garnets are found, and the innermost part of some of the mica crystals consists of unchanged garnet, there can be no doubt that the mica crystals, which have the crystalline form of the garnet, owe their origin to a true pseudomorphosis. Comparing the experi-

mentally determined composition of the unchanged garnets and of a mica crystal, we find that the less soluble compounds, ferrous oxide, and the oxides of manganese, calcium, and magnesium have been replaced by the more soluble oxides of potassium and sodium.

Another pseudomorphosis is that of augite into talc crystals, which have been found in two distinct stages of conversion near Nordre Olafsby, in Sarum.

Some of these crystals, most of which are about 3 centimeters long and 1 centimeter broad, still cleave in one direction, possess a greenish black colour, are transparent along their edges, and are not very hard. Other crystals have lost their capability of cleaving, are grey, and possess the same hardness as talc. In some crystals there is found a nucleus which is still in the first stage of transformation. The chemical change involved in this latter pseudomorphosis consists in the replacement of ferrous oxide and calcium oxide by water and magnesia.

R. S.

Bromine and Iodine in Apatite. By F. Kuhlmann (Compt. rend., lxxv, 1678).

Calcium phosphate from the beds in the departments of Lot and of Tarn-et-Garonne, gave, when treated with sulphuric acid for the manufacture of superphosphate, violet vapours of iodine. The distillate, treated for bromine by Bouis' process, appeared to contain only faint traces of that element. The phosphate will probably be utilized as a commercial source of iodine.

C. G. S.

Meteorite from Bandong, Java. By Daubrée (Compt. rend., lxxv, 1676).

This stone, weighing 2,240 grams, fell with five others on Dec. 10th, 1871. It is an irregular rounded fragment, of sp. gr. 3·519, with a dull blackish surface, presenting numerous spherical indentations. The fracture shows a pale grey stony matrix of silicates, in which are distinguished metallic grains of three different kinds. The first, of an iron-grey colour, consist of nickeliferous iron; others, of a bronze-yellow and iridescent, are iron sulphide; and a third kind, black and insoluble in hydrochloric acid, are chromic iron. Under the microscope a thin section of the matrix is crystalline and transparent.

Analysis gave the following results:—

Soluble in Hydrochloric Acid, 60·17 *p. c.*

S.	Fe.	Ni.	Co.	MnO.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	Al_2O_3.	SiO_2.
2·13	4·95	1·03	0·14	0·12	16·87	12·81	0·30	0·89	0·70	1·43	17·25 = 58·62

Insoluble in Hydrochloric Acid, 39·83 *p. c.*

Chrome-iron.	MnO.	Fe_2O_3.	MgO.	CaO.	K_2O.	Na_2O.	Al_2O_3.	SiO_2.
4·41	trace	4·30	0·43	0·76	0·18	1·40	2·53	20·40 = 34·50
								93·12

Hence the author infers that the meteorite consists of—

Nickeliferous iron.	Iron sulphide.	Chrome-iron ore.	Peridote.	Augite.	Felspathic mineral.	
2·81	5·44	4·41	47·26	20·98	17·00	= 97·90

C. G. S.

Lithological Analysis of the Meteorite from the Sierra de Chaco.—Mode of Formation of Logronite. By STAN. MEUNIER (Compt. rend., lxxv, 1547—1552).

THE substance of meteoric origin known as *logronite* is especially represented by two meteorites of identical composition, one from the Sierra de Chaco (Chili), the other from Logrono (Spain). It consists of a mixture of magnesian silicates interspersed with metallic grains of nickeliferous iron. Mineralogically it does not differ essentially from the generality of meteorites, but is at once distinguished by its structure and external characters, that is to say, by its mode of formation.

The lithoïdal portion of logronite may be mechanically divided into four principal constituents, but the fragments so separated do not differ greatly in composition: they consist essentially of peridote mixed with pyroxene, the former being invariably ferruginous, the latter often containing lime.

The metallic portion of logronite is even less complex in composition than the earthy portion. The two nickeliferous irons known as kamacite and tœnite are easily distinguishable, and since analysis shows the presence of sulphur and phosphorus, it is probable that troïlite and schreibersite are also present. It is noticeable, however, that while a portion of the metal occurs in the shape of rounded grains, another portion assumes a peculiar branching form, and particular attention is directed to this latter structure, since it lends material assistance in the correct interpretation of the question respecting the mode of formation of this mineral.

The various lithological elements of logronite have not a common origin: the author therefore considers it as a true breccia, of which the ramose nickeliferous iron constitutes the cement. He bases his opinion upon the experience obtained in the examination of other polygenic meteorites, and also in the fact that a similar structure is observable in the metallic portions of such breccias as those of Atacama and Brahin; the mineral constitutes, in fact, a bond of union between the purely clastic meteorites and the concretionary breccias properly so called.

Many of the lithoïdal masses of logronite bear distinct evidence of metamorphic modification; and the broken fragments, at first separated from each other, and then soldered together by a metallic emanation, show that the formation of the mineral must have been attended with considerable pressure. In this latter point also the structure is strictly analogous to that of many well-known terrestrial specimens.

J. W.

The Liebfrauensee of Kissingen. By C. Bender (Deut. Chem. Ges. Ber., v, 842—845).

The author has made some analyses of the gas from springs beneath the churchyard at Kissingen. The gas evolved from the water consists of 84·6 parts nitrogen and 15·4 parts oxygen. The gas which is dissolved in the water after the absorption of the carbonic anhydride consists of 74·7 parts nitrogen, and 25·3 parts oxygen. It is seen that these two samples of gas added together in equal quantities will yield almost exactly normal atmospheric air. The quantity of gas absorbed in the water is so considerable that the author considers that the water and gas have been in contact under the pressure of at least three atmospheres. He enters into some detail as to the method of collection of the gas, &c., and of the apparatus for taking the temperature of the water, but no analytical details are given.

A. P.

Analyses of the Mineral Waters of Mehadia in Hungary. By F. C. Schneider and J. Köttsdorfer (Wien. Akad. Ber., lxiv [2], 577—622).

The springs of the Hercules bath, known also as the baths of Mehadia, are situate a short distance from the village of Mehadia, in Hungary, on the borders of Wallachia, about 550 feet above the level of the sea.

Besides the spring which supplies the Hercules bath (which is free from sulphur, and by far the most copious in its flow), there are in the immediate neighbourhood numerous others, all of which contain sulphur-compounds. At the present time the waters of nine springs are used for remedial purposes.

The original memoir gives minute details of the geology of the district, of the history of the springs, and of their individual peculiarities; and the data of numerous analyses of the various waters. The following table gives the mean temperatures of the most important springs and the results of analyses as deduced by the authors:—

Name of spring.	Mean temp.	Solid constituents in 10,000 parts (mean).				
		K_2SO_4.	KCl.	NaCl.	NaSH.	$Na_2S_2O_3$.
Herculesquelle	38°	1·82	—	19·00	—	—
Carlsquelle	41·2°	1·77	1·05	12·66	{ Na_2S 0·25 }	—
Ludwigsquelle*	45°	1·515	1·48	17·28	0·24	0·059
Karolinenquelle	33°	0·67	1·93	18·00	0·61	—
Elisenquelle	45°	0·18	3·18	30 56	0·98	—
Kaiserquelle	56·7°	0·35	6·26	29·20	0·84	0·172
Ferdinandsquelle	54·7°	0·16	6·16	29·45	1·00	0·041
Augenbadquelle†	51·5°	1·19	2·25	37·28	0·68	—
Fussbadquelle	44·3°	1·27	2·41	37·35	0·90	—
Franzensquelle	42·3°	0·02	4·32	38·17	1·07	0·047

* In this water were found also 0·075 $MgBr_2$ and 0·002 MgI_2.
† In this water were found also 0·008 $MgBr_2$ and 0·007 MgI_2.

Name of spring	Solid constituents in 10,000 parts (mean)						
	MgCl	$CaCl_2$	$CaSO_4$	$CaCO_3$	SiO_2	Total	
						Calc	Found
Herculesquelle	0·18	11·70	0·48	0·75	0·39	34·32	34·10
Carlsquelle	0·17	8·50	—	0·62	0·31	25·36	25·17
Ludwigsquelle	0·14	9·93	—	0·35	0·43	31·50	31·19
Karolinenquelle	0·28	12·54	—	—	0·38	33·68	34·67
Elisenquelle	0·21	20·78	—	—	0·15	56·18	55·15
Kaiserquelle	0·30	21·36	—	—	0·11	59·12	58·78
Ferdinandsquelle	0·17	23·30	—	—	0·11	60·80	61·16
Augenbadquelle	0·19	25·75	—	—	0·16	68·08	67·86
Fussbadquelle	0·16	25·93	—	—	0·19	68·50	68·09
Franzensquelle	0·27	27·67	—	0·14	0·53	72·26	71·93

The authors have also made analyses of the gases evolved from some of the waters, the results of which are as follow:—

Constituents in 100 parts	Ferdinands-quelle	Augenbad-quelle	Fussbad-quelle	Franzens-quelle
Carbon dioxide	3·03	2·16	3·32	2·61
Marsh gas	55·73	59·17	59·26	50·70
Nitrogen	41·24	38·37	37·18	46·69
Hydrogen sulphide	traces	traces	traces	traces

J. R.

On the Gas used for Inhalation at Inselbad near Paderborn.

By E. v. Meyer (J. pr. Chem. [2], vi, 360—366).

The author has analysed the gas evolved from the Ottilienquelle, in August, 1872. The following are his results per cent.:—

Carbon dioxide	2·34	2·54	2·85
Oxygen	19·21	18·92	18·98
Nitrogen	78·45	78·54	78·17

The gas evolved from the same spring in 1865 was analysed by Carius, who found—

Carbon dioxide	2·90
Oxygen	6·74
Nitrogen	90·36

The author has analysed also the air of the inhalation room (which is supplied with gas from the spring), and finds that it does not differ appreciably from common air. He concludes that if the remedial virtues formerly attributed to the gas were due to the comparatively

small proportion of oxygen and the predominance of nitrogen it contained, it must, in its present condition, be absolutely valueless.

J. R.

Amount of Carbon Dioxide in the Air of the Soil of Munich at Different Depths and at Different Times. By M. v. Pettenkofer (N. Rep. Pharm., xxi, 677—702).

The soil from which the air was taken in these experiments was a calcareous drift soil, containing sand and apparently free from organic matter. No analysis of the soil is given. The air was extracted from the soil by means of five lead tubes, 1 centimeter in diameter, inserted in the soil to the depth of respectively 4, 3, 2½, 1½, and ¾ meters, the other ends of each tube being connected with an aspirator. For each estimation of carbon dioxide, 14 to 18 litres of air was aspirated in about three hours. The experiments, which extended from September, 1870, to October, 1871, showed that the proportion of carbon dioxide in the air of the soil decreased with tolerable regularity from the lowest layer of the soil upwards, and that only the air in the upper layer was at all quickly influenced by the different rates of diffusion and ventilation, brought on by changes in temperature and increase of wind. During the greater part of the period, air was taken at the same time from the depths of 4 and 1½ meters, ten or twelve experiments being made each month. The means of the quantity of carbon dioxide contained in 1000 parts of the air, by volume, in these comparable experiments, are given in the following table :—

1871.	CO_2 in air from depth of 4 meters.	CO_2 in air from depth of 1½ meters.	1871.	CO_2 in air from depth of 4 meters.	CO_2 in air from depth of 1½ meters.
January...	3·461	2·503	June	6·365	7·702
February..	4·176	2 128	July.......	8·072	8·805
March	4·106	2·786	August	16·138	10·387
April	4·197	2·432	September..	14·016	9·937
May......	5·777	5·402	October....	6·462	4·185

Only in the months of June and July did the air from the upper layer of the soil contain more carbon dioxide than that from the under layer. The maximum and minimum quantities in each layer occurred at about the same time.

The largest proportion of carbon dioxide corresponds with the greatest warmth in the upper layer of the soil.

Hydrostatic water was found at a depth of nearly 6 meters from the surface of the soil, and contained an almost constant quantity of ·122 grams of free carbon dioxide per litre. In an experiment, made to find how much carbonic acid this bottom water could yield up to air lying immediately over it, 1034 litres of the water were allowed to drop through 9 litres of air contained in a flask, in the course of 22 hours, at the end of the experiment the air was found to contain 4.41 parts per 1000 of carbon dioxide; the air obtained from the soil at a depth of

4 meters, on the same day, contained 6·52 parts of carbon dioxide per 1000. In a similar experiment, but with 4300 litres of water passing through 7 litres of air, the air from the flask contained 4·54 parts, whilst air from the soil contained 7·03 parts of carbon dioxide per litre. From these experiments and other considerations the author concludes that the carbon dioxide in the air of the soil could not be derived from the bottom water, but that both the air and water of the soil must obtain their carbon dioxide directly from the soil, and suggests that some of the lowest forms of animal life may be the principal source of carbon dioxide in this soil.

E. K.

Volcanic Energy, an attempt to Develop its True Origin and Cosmical Relations. By R. MALLET (Proc. Roy. Soc., xx, 438; Phil. Mag. [4], xliv, 468).

Organic Chemistry.

New Organic Compounds and New Modes of Preparing them. By F. PFANKUCH (J. pr. Chem. [2], vi, 97—116).

Two preliminary notices bearing on the subjects of this paper have previously been referred to in this Journal ([2] ix, 895 and 901).

Cyanoform and Methintricarbonic Acid.—Traces only of cyanoform are obtained by Fairley's method; the main product consists of a brown, tarry mass. Small quantities of cyanoform are formed by heating chloroform with silver cyanide. By carefully regulating the temperature (120°—130°), and the amount of alcohol added to the mixture of chloroform and potassium cyanide, the author has been able to obtain a certain quantity of pure cyanoform; it crystallises from an alcoholic solution on slow evaporation in small, yellowish-white needles, which can scarcely be said to possess a pleasant odour. Cyanoform could not be obtained by heating iodoform with either mercury or silver cyanide, but by digesting with mercury cyanide and alcohol for some hours in sealed tubes at 120°, it was entirely converted into a double compound of the formula, $[CH(CN)_3]_2(HgI_2)_3$. By treatment with ammonium sulphide this compound is converted into the corresponding ammonium double salt, $CH(CN)_3(NH_4I)_3$, crystallising in small, deliquescent cubes. The author does not appear to have succeeded in isolating pure cyanoform from the above mercury double salt; he remarks that it is most difficult to separate the iodine entirely from the cyanoform. Cyanoform is readily converted into *methintricarbonic acid*, by heating either with soda or with hydrochloric acid solution. This acid crystallises in small needles; an analysis of it agreeing well with the formula, $CH(CO_2H)_3$, is quoted. The normal sodium salt $CH(CO_2Na)_3$ is precipitated on the addition of soda solution to a not too weak aqueous solution of the acid; it forms most brilliantly glistening plates. This also was analysed. The barium salt is finely crystalline, and almost insoluble in water. The silver salt, $CH(CO_2Ag)_3$, is

non-crystalline; a silver determination gave 69·1; the formula requires 69·0.

Sulphoform.—Chloroform acts with explosive violence on an alcoholic solution of potassium sulphide; and alcohol extracts from the product a double compound of sulphoform and potassium sulphide, crystallising in long prisms. No formula is assigned to this compound.

New modes of forming Hydrocarbons.—In describing the production of diphenyl by distillation of a mixture of potassium phenate and benzoate (*Chem. Soc. J.* [2], ix, 895), the author notes that the yield, which is not small, depends on the dryness of the salts employed, and more especially on the proportion in which they are taken; it is desirable to employ a considerable excess over the equivalent quantity of benzoate, although less than double the amount theoretically required should be taken, otherwise the formation of benzophenone interferes with the purification of the product.

The dry distillation of a mixture of potassium phenate and valerate yielded isobutylbenzene (boiling point, 160°). A mixture of potassium chlorobenzoate* and phenate gave monochlorodiphenyl, $C_{12}H_9Cl$ (melting point, 89°). Similarly a mixture of potassium acetate and tribromophenate gave tribromotoluene, $C_7H_5Br_3$, which crystallises from alcohol in small white needles, melting at 150°.

New modes of action of Sulphur.—In addition to the results already referred to (*Chem. Soc. J.* [2], ix, 895), the following require mention:—The author states that the yield of tolane, $C_{14}H_{10}$, on distilling sulphur with barium benzoate, is at least 90 per cent. of that indicated by theory. He enters at length into a description of the mode of purifying the crude product, which contains much tolane sulphide, by copper reduced from the oxide. By distilling a mixture of barium acetate and sulphur, and subsequently removing the sulphur from the product by copper or lead, a liquid hydrocarbon of the composition C_4H_6† (divinyl) was obtained; it is a light oil, which is characterised by an exceedingly sharp, persistent, but not unpleasant odour; the product analysed boiled at about 20°.

These results led the author to examine the action of the metallic sulphocyanates on the metallic salts of acids, such as the benzoic, acetic, &c., in the hope of obtaining organic cyanides. By dry distillation of a mixture of barium benzoate with sulphocyanate in excess, a partially solid distillate was obtained, consisting of benzonitrile, tolane, and new hydrocarbon cyanide; the latter proved to be a mixture of a liquid and a solid compound, neither of which could be obtained in a state of purity. From the still impure liquid compound an acid was obtained by treatment with potash solution, &c., which gave on analysis numbers agreeing with the formula, $C_6H_5.C.CO_2H$. This acid the author terms *benzacrylic acid*. It crystallises in small, glistening needles, which melt at 101°; it is a far stronger acid than benzoic, though less stable.

The acid formed by similarly treating the solid cyano-product could not be prepared perfectly pure; it appears, however, to be identical with an

* The chlorobenzoic acid was prepared by direct chlorination of benzoic acid.

† Analysis gave: carbon, 88·61; hydrogen, 11·30 — required: carbon, 88·9; hydrogen, 11·1.

acid formed on heating the product of the action of cyanogen on an alcoholic solution of tolane with potash. Both the liquid and the solid cyano-compounds appear to be formed by passing tolane vapour over heated mercury or silver cyanide; probably their composition is represented respectively by

$$C_7H_5CN \text{ and } C_{14}H_{10}(CN)_2.$$

Analogous products are formed on distilling lead acetate with lead sulphocyanate; acetonitrile, divinyl, and about 50 per cent. of new cyanogen-compounds are obtained. The latter decompose partially on distillation; the portion first collected, an oil insoluble in water, gave sodium acrylate and ammonia on treatment with soda-solution. The formation of acrylate was demonstrated by the preparation and analysis of the well characterised silver salt.

It is evident from the above that this paper contains a large number of results of the highest interest, and it is to be hoped that no time will be lost in elaborating and confirming them; the descriptions in many cases are unfortunately brief.

H. E. A.

Preparation of Organic Chlorine-compounds. By GRIMAUX (Bull. Soc. Chim. [2], xvii, 3).

THE author makes use of a solution of chlorine in chloroform (a kilogram of chloroform appears, from preliminary experiments, to dissolve 280 grams of chlorine at 0°, and 250 grams at 10°). This solution converts benzene into the hexchloride, $C_6H_6Cl_6$, and naphthalene into the tetrachloride, $C_{10}H_8Cl_4$.

Carbon Chlorides. By K. HOCH (J. pr. Chem. [2], vi, 95—96).

TETRACHLORETHYLENE (C_2Cl_4) was gradually added to a well-cooled mixture of concentrated sulphuric and red fuming nitric acid. The products were nitryl chloride and *nitrotrichlorethylene*. The latter, however, could not be separated in the pure state, owing to its instability; it is a yellow liquid, possessing an extremely intense and unpleasant odour, and causing headache and tears; it is decomposed by water and alkalis. By heating with bromine for some hours at 140°—150°, it is converted into $C_2Cl_3(NO_2)Br_2$; a crystalline substance, melting at about 120°, with decomposition (separation of bromine), easily soluble in ether, less soluble in alcohol. By heating with liquid nitric peroxide in sealed tubes at 115°, it is converted into *trinitrotrichlorethane*, $C_2Cl_3(NO_2)_3$, which crystallises in feathery forms; this body is not explosive, but gives up nitric peroxide on heating.

H. E. A.

Correction of some Erroneous Statements concerning the Production of Chloroform. By A. BELOHOUBEK (Ann. Chem. Pharm., clxv, 249).

LIEBEN has shown that *pure* methylic alcohol, acetic acid, &c., yield no iodoform, whereas ethyl alcohol, aldehyde, acetone, &c., do produce

this substance under suitable circumstances. The author finds that whilst a considerable quantity of chloroform is obtainable from wood spirit purified in the ordinary way, by treating it with bleaching powder and water, *none whatever* can be formed from pure methylic alcohol obtained from the crystalline oxalate, when subjected to this treatment. Similarly no chloroform is obtainable from methyl oxalate, or from acetic acid when treated with *aqueous* bleaching powder (the production of chloroform on heating *dry* acetates with bleaching powder might be expected, as acetone would be first formed). Probably, therefore, bodies which do not yield iodoform will not produce chloroform.

C. R. A. W.

Action of Ether upon Iodides. By E. Ferrière (J. Pharm. Chim. [4], xvi, 107).

When a concentrated solution of an iodide is mixed with starch-paste and then shaken with ether, part of the iodine is separated, and the starch is turned blue. If the solution is dilute, the blueing does not appear till after two or three hours, and in extremely dilute solutions not till after two or three days. On filtering from the blue starch and adding more ether, a blue colour is again produced, and so on, till at length all the iodine is removed from the compound. Mineral waters containing iodides exhibit, when thus treated, the same reactions as artificially prepared solutions.

H. W.

New Propyl Derivatives. By A. Cahours (Compt. rend., lxxvi, 133).

Propyl Sulphide.—This compound is readily obtained by heating potassium monosulphide with iodide or chloride of propyl in alcoholic solution, the action being completed at the temperature of the water-bath in sealed tubes. Most of the alcohol is evaporated off, and the residue treated with water, which leaves undissolved a fœtid oil lighter than water, boiling at 130°—135° after desiccation with anhydrous calcium chloride, and of specific gravity 0·814 at 17°.

When treated with propyl iodide and a little water in sealed tubes, this sulphide gives rise to a sulphino-iodide, $S\begin{cases}C_3H_7\\C_3H_7\\C_3H_7\\I\end{cases}$; when this iodide is treated successively with silver oxide, hydrochloric acid, and platinum chloride, it yields a platino-chloride of formula—

$$\{S(C_3H_7)_3Cl\}_2PtCl_4.$$

Similarly, propyl iodide combines with the sulphides of ethyl and methyl, giving rise to the compounds—

$$S\begin{cases}C_3H_7\\C_2H_5\\C_2H_5\\I\end{cases} \text{ and } S\begin{cases}C_3H_7\\CH_3\\CH_3\\I\end{cases}.$$

which form the platinochlorides—

$$\{S(C_3H_7)(CH_3)_2.Cl\}_2PtCl_4 \text{ and } \{S(C_3H_7)(C_2H_5)_2Cl\}_2PtCl_4,$$

and the iodides of ethyl and methyl combine with propyl sulphide to form analogous compounds.

Mercury-propyl.—When propyl iodide is treated by Frankland and Duppa's process (action of sodium amalgam in presence of acetic ether), mercury-propyl is obtained forming a liquid insoluble in water, slightly soluble in alcohol, and readily soluble in ether, boiling at 189°—191°, and having the specific gravity 2·124 at 16°. Iodine and bromine combine with this substance with great energy, producing crystalline compounds crystallisable from alcohol.

Zinc-propyl is formed by acting on mercury-propyl with zinc at 100°—120°, or by treating propyl iodide with an alloy of zinc and sodium.

Aluminium-propyl is produced by acting on mercury propyl with thin aluminium foil at 120° in sealed tubes; it distils in hydrogen at 240°—245°, and is decomposed by water with production of gelatinous alumina.

Stannopropyl Compounds.—On treating propyl iodide with tinfoil or with an alloy of tin and sodium, *stannotripropyl iodide* $Sn(C_3H_7)_3I$ is formed, eight or ten hours heating in the water-bath in sealed tubes being sufficient. The contents of the tube are treated with ether, and the ethereal solution of the tin-compound is distilled. A liquid boiling at 265°—272°, then passes over, which by rectification easily yields pure stannotripropyl iodide, boiling at 269°—270°. On heating this with strong potash-solution, *stannotripropyl hydrate*, $Sn(C_3H_7)_3(OH)$,* is obtained as a heavy oil, which concretes on standing to a magnificently crystallised mass made up of interlaced prisms having an alkaline reaction; this substance is dehydrated by distillation with caustic baryta, forming *stannotripropyl oxide*—

$$Sn_2(C_3H_7)_6O = \left.\begin{matrix}Sn(C_3H_7)_3\\ Sn(C_3H_7)_3\end{matrix}\right\}O,$$

which is reconverted into the hydrate by addition of water; sulphuric acid forms with this oxide a compound but little soluble in water, but crystallisable in fine prisms from alcohol; similarly acetic, formic, butyric acids, &c., form well-crystallised compounds, which much resemble the corresponding substances in the stannotriethyl and stannotrimethyl series.

Stannotripropyl cyanide is obtained as a crystalline sublimate by heating in a tube sealed at one end a mixture of stannotripropyl iodide and silver cyanide.

Nitropropane.—Iodide of propyl acts on silver nitrite at the ordinary temperature, heat being evolved; the action is complete in a short time on the water-bath; the contents of the sealed tubes employed being distilled in an oil-bath, a liquid boiling at 125°—128° can be readily isolated from the distillate. This product is isomeric with propyl nitrite, and is apparently the homologue of the nitroethane,

* The analogous compound $Si(C_2H_5)_3(OH)$ having been termed triethyl silicol by Ladenburg, this substance might be conveniently named *tripropyl stannol;* the stannotripropyl oxide being the ether corresponding to this variety of tertiary alcohol.—C. R. A. W.

nitromethane, and nitropentane similarly obtained by Meyer and Stüber from ethyl, methyl, and amyl iodides respectively; nascent hydrogen converts this compound into propylamine; and a solution of soda in absolute alcohol yields the compound $C_3H_6Na(NO_2)$. Hence, without doubt, the liquid is nitropropane, $C_3H_7(NO_2)$, *i.e.*, the nitro-derivative of propane, C_3H_8. A solution of iodine in potassium iodide similarly appears to give rise to the compound $C_3H_6I(NO_2)$.

C. R. A. W.

Isopropylic Ethers. By R. SILVA (Bull. Soc. Chim. [2], xvii, 97).

Isopropyl formate, $C_3H_7.CHO_2$, prepared by the action of isopropyl iodide on cupric acetate at 120°, boils at 65°—67° (bar. at 44·7 mm.). The *cyanate*, C_3H_7,CNO, obtained by treating the iodide with silver cyanate, boils at 74°. *Mono-isopropyl lactate*, $C_3H_7.C_3H_4(OH)O_2$, obtained by heating lactic acid with isopropyl alcohol, boils at 166°—168°. *Di-isopropyl lactate*, $(C_3H_7)_2.C_3H_4O_3$, formed by the action of isopropyl iodide on the sodium derivative of the preceding ether, boils at a slightly higher temperature. H. W.

Normal Butyl Compounds and Valerianic Ether. By A. LIEBEN and A. ROSSI (Ann. Chem. Pharm., clxv, 109).

NORMAL butyl iodide was treated with sodium butylate; in the cold but little action took place, but on heating the materials in a flask with inverted condenser, some butylene was evolved and a quantity of *butyl ether* formed:

$$C_4H_9ONa + C_4H_9I = \begin{cases} NaI + C_4H_9OH + C_4H_8 \\ NaI + (C_4H_9)_2O. \end{cases}$$

After repeated distillations over sodium the normal butylic ether was found to boil at 140·5° at 741·5 mm. (corrected and reduced to 0°).

In a similar manner *butyl carbonate* was prepared from silver carbonate and the iodide; by fractional distillation a pure product boiling at 207° at 740 mm. was isolated, the following reactions also taking place, whereby butyl ether and alcohol were formed:—

$$2C_4H_9I + Ag_2CO_3 = \begin{cases} 2AgI + (C_4H_9)_2CO_3 \\ 2AgI + (C_4H_9)_2O + CO_2 \\ 2AgI + C_4H_9.OH + C_4H_8 + CO_2. \end{cases}$$

Fermentation butyl carbonate boils at 190° (Wurtz), or about 17° lower than the normal ether.

Tributylamine was prepared by heating with butyl iodide and alcohol the mixture of primary, secondary, and tertiary amines obtained as a bye-product in the synthesis of normal valerianic acid from butyl cyanide; after boiling with caustic potash *tetrabutylammonium iodide* and *tributylamine* were formed: the former was not attacked by boiling caustic potash, but was soon decomposed by moist silver oxide; the latter boiled between 211° and 215° (corrected) at 740 mm. (the tributylamine from fermentation alcohol boils about 30° lower), and

formed a crystalline hydrochloride from which caustic potash or ammonia precipitated the base as an oily liquid.

The barium salt of butylsulphuric acid was prepared by adding sulphuric acid gradually to the cooled alcohol, diluting the product with water, neutralising with baryta-water, crystallising the barium salt, and drying over sulphuric acid; it has the formula $Ba(SO_4.C_4H_9)_2H_2O$, and is stable at 60°, but decomposes at 100°.

Normal ethyl valerate was prepared from the acid by the action of sulphuric acid and alcohol; it boils at 144·6° (corrected) at 736·5 mm., or 10° higher than the ether of ordinary valerianic acid.

The specific gravities of some of the foregoing compounds were found to be—

	At 0°.	20°.	40°.
Normal butyl ether......	0·784	0·7685	0·7555
„ butyl carbonate..	0·9407	0 9244	0·9111
„ tributylamine....	0·791	0 7782	0·7677
„ ethyl valerate....	0·894	0·8765	0·8616

The difference in boiling point between corresponding normal and fermentation butyl-compounds containing the butyl groups *once* in their formulæ respectively, is about 8° or 10°; and a difference twice as great is noticed between the boiling points of corresponding compounds whose formulæ contain *two* butyl groups (*e.g.*, the carbonic ether), and three times as great when *three* butyl groups are present (*e.g.*, the tributylamines).

C. R. A. W.

Production of Tertiary Butyl Chloride from Butylene. By D. SALESSKY (Ann. Chem. Pharm., clxv, 92).

ISOBUTYLENE is not absorbed by concentrated aqueous hydrochloric acid; tubes filled with very strong acid-solution were cooled by a powerful freezing mixture, and isobutylene was condensed in them; after sealing up they were heated to 100° for several hours; on opening no pressure was noticed, but an oily layer of nearly pure tertiary butyl chloride was formed: this was recognised by its boiling point and the production of trimethylcarbinol from it by the long-continued action of hot water. Hence the reaction is—

$$\begin{array}{l} C(CH_3)_2 \\ \| \\ CH_2 \end{array} + HCl = \begin{array}{l} C(CH_3)_2.Cl \\ | \\ CH_3, \end{array}$$

and not

$$\begin{array}{l} C(CH_3)_2 \\ \| \\ CH_2 \end{array} + HCl = \begin{array}{l} C(CH_3)_2.H \\ | \\ CH_2.Cl, \end{array}$$

as might have been expected.

C. R. A. W.

Properties of Trimethyl Carbinol. By A. BUTLEROW (Ann. Chem. Pharm., clxii, 228).

PURE anhydrous trimethyl carbinol is solid and crystalline at ordinary temperatures, and melts and solidifies at 25·0°—25·5°; it frequently remains fluid on cooling after melting, but crystallises by agitation. Traces of water lower the melting point very much, a mixture of 10 parts trimethyl carbinol and 1 of water remaining liquid at 0°, but crystallising in a bath of snow and salt. It is deliquescent, and is only dehydrated with difficulty, caustic baryta being the best dehydrating agent. When pure and dry it boils at 82·5° at 750 mm. pressure, and has the specific gravity 0·7788 at 30°, its coefficient of expansion for 1° being 0·00136 between 30° and 50°.

When quickly cooled from the liquid state, it crystallises in needle-shaped prisms often joined at angles of 120° or 160°; by slow cooling of the somewhat moist liquid, large transparent six-sided prisms are obtained, truncated by the basal face: they exhibit two axes of double refraction, and are, in fact, rhombic prisms of 120°, combined with the brachypinacoïd and the base. The plane of the optic axes is parallel to the base, and the medium line is perpendicular to the plane of the brachypinacoïd.

Trimethyl carbinol forms a hydrate, $2C_4H_{10}O.H_2O$, which boils constantly at 80°, and is fluid at 0°, but solidifies in a freezing mixture (this hydrate, therefore, resembles the analogous isopropyl alcohol hydrate obtained by Erlenmeyer). The specific gravity of this hydrate is 0·8276 at 0°, and its coefficient of expansion 0·00108 between 0° and 30°: the calculated specific gravity would be 0·8247; so that considerable contraction takes place in the formation of this hydrate; a still greater contraction takes place in the formation of the hydrate $C_4H_{10}O.H_2O$, which does not solidify.

To dissolve trimethyl carbinol at 0°, about 9 per cent. of its weight of water must be added (8·9 and 9·4 parts in two experiments).

C. R. A. W.

Conversion of Amylene into an Amyl Alcohol by Sulphuric Acid. By FLAVITSKY (Ann. Chem. Pharm., clxv, 157—158).

BERTHELOT found that small quantities of amylene hydrate were formed by the action of sulphuric acid upon amylene, but Erlenmeyer observed only the formation of diamylene by this reagent. Now isobutylene is also readily polymerised by sulphuric acid, but nevertheless Butlerow has succeeded in converting it into trimethyl carbinol by this acid. The author, therefore, employing Butlerow's continuous process (Russ. Chem. Ges. Zeitschr., 1870, 106), endeavoured, and with success, to hydrate amylene. He conducted a slow stream of carbon dioxide charged with amylene vapour into a mixture of two parts of sulphuric acid and one of water. Part of the amylene was converted into diamylene, but the rest dissolved, and from this solution on the addition of water an alcohol separated. This alcohol boiled, however, between 100° and 108°, and repeated fractional distillation failed to yield amylene hydrate. More than half boiled at 102°—104°. By oxi-

dation with dilute sulphuric acid and potassium chromate, the alcohol yielded only common acetone, not methyl-pseudopropyl-ketone. It may have consisted in part of dimethylethyl carbinol (tertiary amyl alcohol).

E. D.

Identity of the Hexyl Compounds from Mannite and Dulcite. By OTTO HECHT (Ann. Chem. Pharm., clxv, 146—156).

SOME doubt has been raised as to the identity of the hexyl iodide obtained from melampyrite with that obtained from mannite. Fittig considers mannite and dulcite to be thus constituted—

Mannite $CH_2OH—CHOH—CHOH—CHOH—CHOH—CH_2OH$.

Dulcite $\begin{matrix} CH_2OH \\ CH_2OH \end{matrix}\Big\rangle COH—CHOH—CHOH—CH_2OH$,

the two iodides being—

Hexyl iodide, from mannite $CH_3—CH_2—CH_2—CH_2—CHI—CH_3$.

Hexyl iodide, from dulcite $\begin{matrix} CH_3 \\ CH_3 \end{matrix}\Big\rangle CH—CH_2—CHI—CH_3$.

The author has, at the instance of Prof. Erlenmeyer, made a thorough investigation of these iodides and their derivatives. He finds them to be identical, and to have the constitution given above to the iodide from mannite. The boiling points and specific gravities of the two iodides, hexylenes and hexylalcohols, are respectively identical, or nearly so, and the alcohols both yield acetic acid and normal butyric acid when oxidised by chromic acid.

E. D.

Preparation of Crystallised Grape-Sugar. By H. SCHWARZ (Dingl Polyt. J., ccv, 427—429).

THE author observed that cane-sugar immersed in alcohol acidulated with hydrochloric acid slowly dissolved, and that the walls of the vessel became coated with crystallised grape-sugar, from which he concludes that in cold alcoholic solutions the formation of grape-sugar takes place directly, and not by change of invert sugar under the influence of time and light, as is the case when hot aqueous solutions are used.*

C. H. G.

Action of Sulphuric Acid on Cellulose. By A. TERREIL (Bull. Soc. Chim. [2], xvii, 3).

CELLULOSE dipped into a 1 p. c. solution of potassium iodide, then, after drying, into strong sulphuric acid, and washed with water, is converted

* It is fully established that when cane-sugar is inverted, both right and left-handed glucoses are formed at once, though the dextrose crystallises out of the mixture very slowly. In the above case the cellulose doubtless remained in solution.—C. H. G.

into a blue substance, which is different from iodide of starch, and exhibits blue and red globules under the microscope.

H. W.

The Hydrates of the Fatty Monobasic Acids. By E. GRIMAUX (Bull. Soc. Chim. [2], xviii, 535—547).

THE so-called theory of atomicity not being able to account for the existence of numerous compounds, especially those containing combined water (of crystallisation or otherwise), such substances are conveniently termed *molecular combinations*, a peculiarly happy phrase, inasmuch as it permits of the existence of bodies inexplicable by atomicity, and yet gives no satisfactory explanation of their constitution. Numerous bodies of this class ordinarily known as "molecular compounds" of water and other substances, have quite as much right to be considered "atomic compounds" as any other substances ordinarily recognised as belonging to the latter class. Thus definite compounds of water with formic, acetic, valeric, &c., acids, are known; it is true they have but little stability, but in this respect they only differ in degree from the perchloride of phosphorus, the hydriodide of propylene (iodide of isopropyl), and analogous compounds. The true formulæ of these so-called hydrates are—*formyl-carberin*, $CH\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$ = hydrate of formic acid = $CHO(OH) + H_2O$; *acetyl-carberin*, $CH_3.C\left\{\begin{matrix}OH\\OH\\OH\end{matrix}\right.$ = hydrate of acetic acid = $CH_3.CO.OH + H_2O$, &c., &c. The term *carberin* may be conveniently applied to those varieties of glycerins which are distinguished from other glycerins by having *three hydroxyl groups in association with the same carbon atom.*

By analogy with glycerins, these substances should form monoacetins and analogous bodies, which in fact exist; thus, $CH_3.C\left\{\begin{matrix}O.C_2H_3O\\OH\\OH\end{matrix}\right.$ is the mono-acetin of acetyl carberin; and a body of this formula is well known, being simply the ordinary form of acetic acid, which (as shown by Cahours, Bunsen, Playfair and Wanklyn) has the formula $C_4H_8O_4$, the simpler formula $C_2H_4O_2$ being possessed only by the vapour when heated considerably above its boiling-point. Similarly $CH\left\{\begin{matrix}O.COH\\OH\\OH\end{matrix}\right.$, or ordinary formic acid, may be viewed as the mono-formin of formyl carberin, and similarly with butyric and valeric acids (Cahours). The compound acids, acetobutyric, acetopropionic, &c., are similarly constituted, and the diacetate of potassium, the acid trichloracetates, bibenzoates, &c., may be viewed as derivatives from similar bodies.

Diacetate of potassium.	Acetobutyrate of silver.
$CH_3.C\left\{\begin{matrix}O.C_2H_3O\\OH\\OK.\end{matrix}\right.$	$CH_3.C\left\{\begin{matrix}O.C_4H_7O\\OH\\OAg.\end{matrix}\right.$

The trichlorhydrins corresponding to those carberins are known, viz., $CH.Cl_3$ (chloroform), $CH_3.CCl_3$ (chlorinated ethyl chloride—Geuther), &c., &c.; similarly the triethylins, $CH(O.C_2H_5)_3$ (Kay's ether), and $CH_3.C(O.C_2H_5)_3$ (prepared by Geuther from the corresponding trichlorhydrin and sodium ethylate), &c., &c.

The ordinary acids $(C_nH_{2n}O_2)_2$ may, however, be viewed in another light, viz., as bearing the same relation to the carberins that pyroglycide does to glycerin—

Diacetic acid (ordinary acid). Pyroglycide.

$$CH_3 . C(OH) \left\{ \begin{matrix} O \\ O \end{matrix} \right\} C(OH) . CH_3. \quad CH(OH) \left\{ \begin{matrix} CH_2 . O . CH_2 \\ CH_2 . O . CH_2 \end{matrix} \right\} CH(OH),$$

the following series being strictly comparable.

Glycerin,	Glycide (unknown).	Pyroglycide.	Glycerylin.
$C_3H_5.(OH)_3$.	$C_3H_5 \left\{ \begin{matrix} O \\ OH. \end{matrix} \right.$	$\begin{matrix} C_3H_5 \\ C_3H_5 \end{matrix} \left\{ \begin{matrix} OH \\ O_2 \\ OH. \end{matrix} \right.$	$\left. \begin{matrix} C_3H_5 \\ C_3H_5 \end{matrix} \right\} O_3.$
Phosphoric acid.	Metaphosphoric acid.	Madrell's sodium metaphosphate.	Phosphoric anhydride.
$PO.(OH)_3$.	$PO \left\{ \begin{matrix} O \\ OH. \end{matrix} \right.$	$\begin{matrix} PO \\ PO \end{matrix} \left\{ \begin{matrix} ONa \\ O_2 \\ ONa. \end{matrix} \right.$	$\left. \begin{matrix} PO \\ PO \end{matrix} \right\} O_3.$
Acetyl carberin (hydrated acid).	Acetic acid (at 230°) (dissociated acid).	Diacetic acid (ordinary acid).	Acetic anhydride.
$C_2H_3.(OH)_3$.	$C_2H_3 \left\{ \begin{matrix} O \\ OH. \end{matrix} \right.$	$\begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix} \left\{ \begin{matrix} OH \\ O_2 \\ OH. \end{matrix} \right.$	$\left. \begin{matrix} C_2H_3 \\ C_2H_3 \end{matrix} \right\} O_3.$

The only objection that can be raised to the views proposed is that the dogma has been laid down that it is impossible for more than one hydroxyl group to be in association with the same carbon-atom; but, without reckoning the glyoxylates, the mesoxalates, $\begin{matrix} CO(OM) \\ C(OH)_2 \\ CO(OM) \end{matrix}$, and possibly propylphycite, it is an established fact that the so-called chloral hydrate is a well-marked glycol, $CCl_3.CH(OH)_2$, forming chlorhydrins, a chlorethylin, ethylins, &c., &c., like ordinary glycols; so that the dogma is not strictly true. At the most, it can only be said that substances of the kind break up readily into water and an anhydride.

C. R. A. W.

Note by Abstractor.—In a paper read at the Brighton meeting of the British Association ("Report on Essential Oils," *British Association Reports*, 1872), the abstractor pointed out that aldehydes and acids containing the group CO.OH are really the anhydrides of glycols and glycerins containing more than one hydroxyl group in connection with the same carbon-atom, alcohols, aldehydes, and acids being formed from hydrocarbons by successive oxidation; thus $X'.CH_3$ being a hydrocarbon—

$$2X.CH_3 + O_2 = 2X.CH_2.OH = \text{Alcohol.}$$
$$2X.CH_2(OH) + O_2 = 2X.CH.(OH)_2 = \text{Ortho-aldehyde.}$$
$$2XCH(OH)_2 + O_2 = 2XC(OH)_3 = \text{Ortho-acid.}$$

Similarly secondary alcohols and ortho-ketones are formed by the oxidation of hydrocarbons $X.CH_2.Y$—

$$2X.CH_2.Y + O_2 = 2X.CH(OH).Y = \text{Secondary alcohol,}$$
$$2X.CH(OH)Y + O_2 = 2X.C(OH)_2.Y = \text{Ortho-ketone,}$$

the ordinary ketones being the anhydrides of the ortho-ketones, which are really glycols containing two hydroxyl groups in association with the same carbon-atom, and are consequently very unstable bodies. Like "chloral hydrate" and the ordinary glycols, the ortho-aldehydes and ortho-ketones form chlorhydrins, ethylins, &c., &c.

See also this *Journal* [2] x, 653, where it is pointed out not only that the hydrate of acetic acid is $CH_3.C(OH)_3$, but that tribasic salts of this acid are known, *e.g.*, lead orthoacetate. Similarly orthosulphuric acid is $S(OH)_6 = SO_4H_2 + 2H_2O$; and crystallised oxalic acid is $\begin{matrix} C(OH)_3 \\ | \\ C(OH)_3 \end{matrix}$ $= C_2H_2O_4 + 2H_2O$. Bourgoin (*Bull. Soc. Chim.* [2], xvii, 244) has lately made experiments from which he infers that when a solution of sulphuric or oxalic acid is electrolysed, the compound decomposed is really $S(OH)_6$ or $C_2(OH)_6$, and not SO_4H_2 or $C_2H_2O_4$, the water taking no part whatever in the action of the current. (See p. 27 of this volume).

C. R. A. W.

Butyric Acid from various Sources. By Carl Grünzweig (Ann. Chem. Pharm., clxii, 193).

The author reviews the various researches on butyric acid, and on substances from which this acid is derivable, that have been previously published by other chemists.

Normal butyric acid, after several fractional distillations over phosphoric anhydride, boils at 157°—160° under a pressure of 716 mm.; it is a colourless liquid, smelling much like acetic acid, and miscible with water in all proportions. The only difference existing between normal butyric acid and isobutyric acid as to the products of their oxidation by chromic acid lies in the fact that the normal acid is much less readily acted on; the actual products, however, are the same in each case, viz. acetic and carbonic acids; in two experiments with the iso-acid, 98·4 and 100·4 per cent. of the theoretical quantity of carbonic acid was obtained, whilst in three experiments with the normal acid 71, 75, and 106 per cent. were respectively obtained.

Silver butyrate, $C_4H_7AgO_2$; *calcium butyrate*, $Ca\left\{\begin{matrix} C_4H_7O_2 \\ C_4H_7O_2 \end{matrix}\right., H_2O$; *strontium butyrate*, $Sr\left\{\begin{matrix} C_4H_7O_2 \\ C_4H_7O_2 \end{matrix}\right., H_2O$; and *zinc butyrate*, $Zn\left\{\begin{matrix} C_4H_7O_2 \\ C_4H_7O_2 \end{matrix}\right.$, $2H_2O$, were examined. The following solubilities were observed:—

	Silver salt.	Calcium salt.	Strontium salt	Zinc salt.
100 parts of water dissolve	0·413 parts at 16°.	18·1 (anhydrous) 19·61 (crystallised) at 22°	39·2 (crystallised) at 20° 40·2 at 22°.	10·7 (crystallised) at 16°.

Isobutyl butyrate, $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CH_2.O.CO.CH_2.CH_2.CH_3$, was prepared from isobutyl alcohol, concentrated sulphuric acid, and normal butyric acid; it boiled at 150°—153° (uncorrected) at 722 mm., and had the specific gravity 0·8798 at 0°, 0·86635 at 16°, 0·81838 at 98·44°.

Isobutyric acid was prepared by the oxidation of the fermentation alcohol, which boiled at 106°—107°. The acid boiled at 149°—151° (uncorrected) at 718 mm. pressure. Its salts exhibit the following compositions and solubilities:—

	Silver salt. $AgC_4H_7O_2$	Calcium salt. $Ca\left\{\begin{matrix}C_4H_7O_2\\C_4H_7O_2\end{matrix}\right.5H_2O$.	Strontium salt. $Sr\left\{\begin{matrix}C_4H_7O_2\\C_4H_7O_2\end{matrix}\right..5H_2O$.	Zinc salt. $Zn\left\{\begin{matrix}C_4H_7O_2\\C_4H_7O_2\end{matrix}\right..H_2O$.
100 parts of water dissolve .	0·928 parts at 16°.	36·0 parts at 18°.	44·1 parts at 17°.	17·3 parts at 19·5°.

Isobutyl isobutyrate, $\left.\begin{matrix}CH_3\\CH_3\end{matrix}\right\}CH.CO.O.CH_2.CH\left\{\begin{matrix}CH_3\\CH_3\end{matrix}\right.$, boiled at 144°—147° at 722 mm. pressure, and had the specific gravity 0·87579 at 0°, 0·86064 at 150°, 0·81192 at 98·4°.

Butyric Acid from Cow's Butter.—Attempts to saponify butter with lime and thus obtain calcium butyrate directly did not succeed; the older method, therefore, of saponifying with potash and decomposing the potassium salt thus produced with calcium chloride was employed. From the crystalline form and solubility of the silver salt (100 parts water dissolve 0·412 parts of salt at 16°), and from the property of the calcium salt to separate in the solid form on heating its cold saturated solution, the substance ultimately obtained was identified as normal butyric acid.

Butyric Acid from Conine.—Schiff obtained conine from *normal* butyric aldehyde, but noticed certain differences between the natural and artificial bases. To see if these are due to difference in the butyl radicals involved, conine was oxidised with chromic acid, whereby much carbon dioxide was evolved; the silver salt of the resulting butyric acid resembled the normal salt in crystalline form, and was soluble to the extent of 0·423 part in 100 of water at 17°. Hence without doubt conine is a normal butyl derivative, and the observed differences between the natural and artificial alkaloids are due to circumstances other than differences in the carbon groups contained.

Butyric Acid from St. John's Bread (Carob).—The acid contained in the fruit of the *Ceratonia Siliqua* distils over with water, the addition of sulphuric acid being unnecessary; a large bulk of water must, however, be distilled before the whole of the acid comes over. 10 lbs.

of St. John's bread yielded 30 grams of an oily acid, consisting of acetic, isobutyric, and caproic acids, with apparently a trace of benzoic acid. All these acids, therefore, exist in the free state in the fruit. The butyric acid was recognized as the *iso-acid* from the crystalline form and solubilities of the silver and calcium salts. When, however, the portion of the fruit left behind on distillation with water is fermented with chalk and cheese, *normal* butyric acid is produced, recognized as such by the solubility of its silver salt and the properties of its calcium salt. Hence the acid obtained by Marsson from St. John's bread by fermenting it with chalk, &c., must have been a mixture of iso-acid and normal acid.

Gorup-Besanez has recently found butyric acid in old fruit of the *Sapinda Saponaria* (soap tree), and considers it probable that it also exists in old tamarinds. The author could only find acetic acid in the latter.

C. R. A. W.

Crude Butyric Acid of Fermentation. By G. B. Grillone (Ann. Chem. Pharm. clxv, 127).

Fermentation butyric acid was prepared by the author himself by allowing a mixture of malt, milk, chalk, and chopped meat to stand for several weeks; the product was heated to 80°, filtered, and precipitated with sodium carbonate: the filtered liquor yielded a considerable layer of crude acid after evaporation to a small bulk, and mixing with sulphuric acid. This crude acid distilled mostly between 156° and 164°, but part came over below 125°, some between 125° and 155°, and a portion boiled up as high as 215°.

The lowest boiling fractions were found to be *acetic acid*, but no satisfactory evidence of the presence of propionic acid could be obtained, thus corroborating the statement of Linnemann (*Ann. Chem. Pharm.*, 160, 224) that this acid is not present in crude butyric acid.

A foot-note, signed *Lieben*, states that probably the body taken for propylic aldehyde obtained by Lieben and Rossi, on distilling crude calcium butyrate with calcium formate (from the formation of which the occurrence of propionic acid in the crude butyric acid used was inferred), was really a mixture of acetone and acetic aldehyde; by treatment with nascent hydrogen impure isopropyl alcohol was formed, which was mistaken for fermentation propylic alcohol.

The higher boiling portions were separated into butyric acid and *caproic acid* boiling between 200° and 205°, the most convenient method being found to be repeated washing with water, which dissolves the former acid with only traces of the latter; the absence of valerianic acid is thus proved. The caproic acid thus isolated yielded an anhydrous barium salt, 100 parts of a saturated solution of which contained at 21° to 22° 8·3 parts of dry salt (normal barium caproate is anhydrous and 100 parts of solution contains, at 18·5°, 8·4 parts of dry salt, whilst the fermentation amyl cyanide yields a caproic acid, the barium salt of which contains $2H_2O$; and 100 parts of solution of this salt contain at 18·5° 34·65 parts of dry salt). The calcium salt similarly contained 1 mol., H_2O, thus corresponding with the normal salt and not

with that of the ordinary acid, which contains $3H_2O$; 100 parts of solution saturated at 21°—22° contained 4·4 of dry salt (the normal salt solution contains 2·7 and the ordinary 11·3 of dry salt at 18·5°).

The author hence considers that the existence of normal caproic acid in fermentation butyric acid is proved.

C. R. A. W.

Purification of Oxalic Acid. By H. HABEDANCK (Zeitschr. anal. Chem., xi, 282).

COMMERCIAL oxalic acid is dissolved in the smallest possible quantity of hot absolute alcohol, filtered, and the acid which separates on cooling is crystallised from water.

To prepare pure ammonium oxalate the alcoholic mother-liquors are diluted with water, heated and neutralised with ammonia. The oxamide and oxamethane which are formed may be destroyed by slightly acidulating the liquor with oxalic acid and boiling it for some time; the liquid should then be made slightly alkaline with ammonia and allowed to crystallise.

T. B.

Ethylmalonic Acid. By J. WISLICENUS and F. URECH (Ann. Chem. Pharm., clxv, 93—98).

ONE of the authors has previously stated (*Ann, Chem, Pharm.*, cxlix, 215) that the potassium salt of the acid obtained from crude cyanobutyric acid (prepared by heating bromobutyric ether with an alcoholic solution of potassium cyanide) by digesting it with potash solution, gave an insoluble lead salt, which, after decomposition by hydrogen sulphide, gave a strongly acid syrup, which partially crystallised. The analysis and melting point (111°—112°) of the solid acid led him to regard it as pyrotartaric acid, and since a lead salt of the same composition as lead pyrotartrate was obtained from the liquid acid, this was regarded as ethylmalonic acid.

It is now found that the liquid acid is merely the solid acid, together with impurities which hinder crystallisation, and the further discovery has been made that the crystalline acid is not pyrotartaric acid, $\begin{cases} CH_3 \\ CH.CO_2H \\ CH_2.CO_2H \end{cases}$, but the isomeric *ethylmalonic acid*, $\begin{cases} CH_2.CH_3 \\ CH_2(CO_2H)_2 \end{cases}$.

Ethylmalonic acid crystallises in prisms, which dissolve with moderate ease in water. Although it has nearly the same melting point as pyrotartaric acid, which melts at 112°, it is readily distinguished therefrom by its behaviour when heated; thus, whereas pyrotartaric acid is converted into the anhydride, ethylmalonic acid is split up into butyric acid and carbonic anhydride, and is therefore strictly homologous with isosuccinic acid.

The zinc, copper, and lead salts of the new acid are described,—the alkali salts yield no precipitate with ferric chloride, whereas the corresponding pyrotartrates yield a red, glutinous precipitate.

H. E. A.

Preparation of Oxymaleic Acid. By E. Bourgoin (Bull. Soc. Chim. [2], xvii, 2).

This acid is obtained by heating bromomaleic acid with bromomaleate of silver.

Pyroracemic Ethers. By A. Oppenheim (Deut. Chem. Ges. Ber., v, 1051).

Pyroracemic acid does not yield an ether by treatment with alcohol and hydrochloric or sulphuric acid.

The author therefore operated upon the silver salt, which he obtained as an extremely bulky gelatinous precipitate, with ethyl iodide diluted with dry ether. A reaction commenced in the cold, but after completing the decomposition by heating to 100°, pyroracemic acid and syrupy condensation products were the only results.

Methyl iodide was employed more successfully, but even in this case much of the acid was liberated. Methyl pyroracemate is a liquid which boils between 134° and 137°, and has a specific gravity 1·154 at 0°.

The smell of this ether is distinctly like that of acetone, and with sodium acid sulphite it became hot, but did not yield a crystalline compound. The author therefore retains the formula, $\begin{cases} CH_3 \\ CO \\ CO.OCH_3 \end{cases}$, which the experiments of Wichelhaus and Klimenko have rendered probable.

W. A. T.

Electrolysis of Itaconic Acid. By G. Aarland (J. pr. Chem. [2], vi, 256—272).

This paper commences with a comprehensive account of previous investigations on the electrolysis of organic compounds and of the conclusions drawn from these investigations.

The author now finds that the acid which he previously submitted to electrolysis (*J. pr. Chem.* [2], iv, 376), consisted principally of citraconic acid and not of itaconic acid, as stated. Itaconic acid was now prepared by the method of Wilon, and mesaconic acid was prepared according to the directions of Swarts, but its melting point was found to be 200·5° and not 208°, as stated in the handbooks.

Reactions of Citraconic acid, Itaconic acid, and Mesaconic acid with ferric chloride. The addition of ferric chloride to a solution of citraconic acid neither gives rise to precipitation nor to coloration; when, however, a solution of this acid is heated with excess of ferric chloride, the liquor assumes a reddish-brown colour, which disappears on cooling, but may be re-produced by renewed heating. Neutral ammonium or sodium citraconate gives a red colour with ferric chloride, and on heating the solution, a precipitate is formed, which redissolves on cooling. A large excess of ferric chloride prevents the formation of this precipitate. Itaconic acid gives a slight coloration, but no precipitate with cold ferric chloride; when, however, excess of this reagent

is used and the solution is heated, a reddish-brown precipitate is produced, which does not redissolve when the solution is cooled. Neutral ammonium or sodium itaconate gives with ferric chloride a brown precipitate soluble in excess of the reagent. This solution, when heated, redeposits the precipitate, which however redissolves as the solution cools. Mesaconic acid is slightly coloured by the addition of ferric chloride, and the solution, when boiled, deposits a gelatinous precipitate, which redissolves on cooling. The addition of a further quantity of ferric chloride prevents its re-solution. Neutral mesaconates of alkali-metal give with ferric chloride a brown precipitate, which is insoluble in excess of the reagent, and does not dissolve on the application of heat. It is suggested that mesaconic acid may be used as an analytical reagent in place of succinic acid.

When a saturated neutral solution of potassium itaconate was subjected to electrolysis, the gases evolved from the positive electrode were found to consist of carbonic acid and a modification of allylene which did not precipitate ammoniacal silver nitrate. It combined with bromine, forming a bromide $C_3H_4Br_2$; and this, when heated with excess of bromine, yielded a crystalline tetrabromide, $C_3H_4Br_4$. During this reaction a small quantity of hydrobromic acid is formed, and from this the author concludes that the allylene bromide is accompanied by propylene bromide. After the electrolysis had proceeded for some time, a modification of allylene capable of precipitating ammoniacal silver solution was evolved. The author attributes this result to the decomposition of mesaconic acid, this acid and acrylic acid being both found in the solution after electrolysis. Although pyrotartaric acid could not be detected among the products, the author considers that it is formed, and that it splits up immediately into propylene, carbonic acid, and hydrogen.

$$C_3H_4(COOH)_2 + 2H = C_3H_6(COOH)_2.$$
$$C_3H_6(COOH)_2 = C_3H_6 + 2CO_2 + 2H.$$

The formation of acrylic acid may be thus represented:—

$$\begin{array}{l} CH_2 \\ | \\ CHCOOH \\ | \\ CHCOOH \end{array} + O_3 = \begin{array}{l} CH_2 \\ CH \end{array}COOH + 2CO_2 + H_2O.$$

Citraconic acid yields on electrolysis an allylene which is still under investigation.

T. B.

A Polymeric Modification of Isobutyl Aldehyde.

By G. A. BARBAGLIA (Deut. Chem. Ges. Ber., v, 1052—1053).

ISOBUTYL aldehyde was prepared by oxidising isobutyl alcohol with a very dilute solution of chromic acid, and afterwards purified by fractional distillation and the use of sodium acid sulphite. The aldehyde so

obtained boiled steadily at 61°—62°. It was kept cold and subjected to a slow stream of chlorine. After a time a white crystalline body made its appearance. This was found to be insoluble in water, but soluble in alcohol and more so in ether; it melted at 59°—60° and solidified at 50°—51°. It was volatile in vapour of water and sublimed easily without decomposition. It contained no chlorine, and analysis led to the formula C_4H_8O. Two concordant determinations of vapour density showed, however, that its molecular weight is expressed by three times this formula—

$$3C_4H_8O = C_{12}H_{24}O_3.$$

The conditions under which this modification of the aldehyde is formed are not yet made out, as by a repetition of the experiment the author has not obtained the same body.

W. A. T.

Monochloracetone. By L. HENRY (Deut. Chem. Ges. Ber., v, 965—968).

GLYCIDIC dihydrochloride, $CH_2 = CCl - CH_2Cl$, is readily converted by the action of concentrated sulphuric acid into *monochloracetone*, $CH_3 - CO - CH_2Cl$, boiling at 118°—120°, which is identical with that obtained by the direct action of chlorine on acetone. By heating it with potassium acetate and alcohol, it yields the corresponding acetate, $CH_3 - CO - CH_2(OC_2H_3O)$, a limpid liquid, boiling at 175°, and having a refreshing smell and bitter taste. The freshly prepared compound has a neutral reaction; but in contact with moist air or water, in which it is readily soluble, it soon assumes acid reaction. Different experiments were made in order to convert this ether into the alcohol $CH_3 - CO - CH_2OH$, which corresponds to pyroracemic acid, but so far only with negative results.

C. S.

Chlorinated Derivatives of Acetone. By E. MULDER (Deut. Chem. Ges. Ber., v, 1007—1011).

THE object of this communication is to prove that dichloracetone and monochloracetone may both be formed by the direct action of chlorine on acetone. The details of their preparation are given, and the derivatives obtained from them are described, together with some new results.

The action of potassium hydrate on dichloracetone gives rise to a glucose-like body similar to that produced by the action of water on lead sulphacetonate, together with a brown substance which, with lead acetate, yields the compound $(C_9H_9O_5)_2Pb$. The formation of these two bodies may be represented as follows:—

$$(1.)\ C_3H_4Cl_2O + 2KHO = C_3H_6O_3 + 2KCl.$$
$$(2.)\ 3C_3H_6O_3 - 4H_2O = C_9H_{10}O_5.$$

By following the method of Riche (electrolysis of a mixture of acetone and hydrochloric acid, portions boiling at 135°—140°, and at

120° were obtained. Both these gave analytical results agreeing with dichloracetone. The portion boiling at 120° is regarded by the author as $CHCl_2.CO.CH_3$. After reference to the action of potassium cyanide on dichloracetone, the remark is made that dichloracetone obtained by the action of chlorine on monochloracetone, and boiling at 120°, also yields a solid mass with solution of potassium cyanide.

Monochloracetone may be formed by the action of hypochlorous acid on acetone. T. B.

Preparation of Potassium Ferricyanide. By FERD. RHIEN (Chem. Centralblatt, 1872, 632).

THE author proposes to add to a cold solution of potassium ferrocyanide sufficient hydrochloric acid to withdraw one atom of potassium from two of the salt. To this mixture is then added a clear solution of chloride of lime, till no ferrocyanide remains unchanged. By estimating the strength of the chloride of lime solution, the proper quantity may be added at once. Any excess of hydrochloric acid is neutralised by chalk.

The first crystals obtained on evaporation are, after washing, perfectly pure. Those obtained afterwards show traces of lime, but are easily purified by recrystallisation. The advantages claimed are (1) That the change is effected at the ordinary temperature; (2) Only one filtration is necessary, and there is no precipitate to wash; (3) That all the ferricyanide, except a very unimportant quantity, is obtained by the crystallisation.

G. T. A.

Lacturamic Acid and Lactyl Urea. By F. URECH (Ann. Chem. Pharm., clxv, 99—103).

PURE alanine was converted into the neutral sulphate, and this was heated in aqueous solution with a slight excess of potassium cyanate; much alcohol was then added, the potassium sulphate removed by filtration, the liquid evaporated, and the crystalline product several times recrystallised from aqueous alcohol.

Lacturamic acid, $\left\{\begin{array}{l}CH_3\\ CH(NH.CONH_2),\\ COOH\end{array}\right.$ thus prepared, forms a white, indistinctly crystalline mass, difficultly soluble in cold alcohol and insoluble in ether; it melts with decomposition at 155°. The copper, lead, and silver salts are described. Heated with hydrochloric acid in a sealed tube at 150° it is resolved in alanine, carbonic anhydride, and ammonia.

On heating alone it is converted into water and *lactyl urea*, $C_4H_6N_2O_2$, the next higher homologue of hydantoïn; this compound crystallises in cauliflower-like crusts, easily soluble in water, insoluble in ether, and melts at 125°.

To this Professor Wislicenus adds a note in which he describes the formation of hydantoic acid from glycocine sulphate and potassium cyanate.

H. E. A.

Cyanocarbonic Ether. By A. WEDDIGE (Jr. pr. Chem., [2], vi, 117).

THIS body is obtained by distilling a mixture of three parts of phosphoric anhydride with two parts of oxamethane, $\begin{cases} CO.NH_2 \\ CO.OC_2H_5 \end{cases}$. It is a colourless mobile liquid, of ethereal but penetrating odour, boiling at 115°—116°; it is almost insoluble in water, but is slowly decomposed thereby, with formation of alcohol, carbonic anhydride, and hydrocyanic acid.

It reacts with an alcoholic ammonia solution, and a white crystalline product is obtained, which the author believes to be the amide of cyanocarbonic acid. H. E. A.

Cyanocarbonic Ether. By L. HENRY (Deut. Chem. Ges. Ber., v, 946—949).

THE author refers to his previous experiments exhibiting the stability of the groups CH_3O, C_2H_5O, etc., towards PCl_3, PCl_5, etc., and mentions how he was thereby led to examine the action of phosphorus pentachloride on oxamethane, hoping thus to obtain cyanocarbonic ether. The experiment has, however, proved unsuccessful. The desired product is no doubt formed, but it is in combination with phosphorus trichloride, and the action of water not only destroys the latter, but also the greater part of the cyanocarbonic ether.

Similarly the action of phosphorus pentasulphide on oxamethane, although giving rise to the formation of a certain quantity of cyanocarbonic ether, proves useless as a method of preparation.

H. E. A.

Allyl Cyanocarbonate. By R. WAGNER and B. TOLLENS (Deut. Chem. Ges. Ber., v, 1045—1047).

THE authors have examined the products of the action of hydrochloric acid upon the dicyanide of allyl alcohol recently discovered by Tollens. They find that with fuming hydrochloric acid the liquid becomes warm, and on the completion of the reaction, the temperature being kept down, a product is formed, from which ammonium chloride and oxamide are deposited in the crystalline form, and on fractional distillation allyl chloride and allyl cyanocarbonate are obtained. This last is a colourless liquid, smelling like mustard, and boiling at 135°.

These bodies are formed, according to the authors, by two simultaneous reactions. In the one, cyanogen is detached from the alcohol and converted into oxamide, whilst the alcohol furnishes allyl chloride—

$$C_3H_5(CN)_2OH + H_2O + HCl = C_3H_5Cl + C_2O_2N_2H_4.$$

In the other, ammonia only is removed, and the carbon of one of the cyanogen groups is linked by means of oxygen to the allyl, forming allyl cyanocarbonate—

$$C_3H_5(CN)_2OH + H_2O + HCl = CN.CO.OC_3H_5 + NH_4Cl.$$

Cyanocarbonic acid is intermediate between oxalic acid and cyanogen—

$$\begin{cases} CO.OH \\ CO.OH \end{cases} \qquad \begin{cases} CN \\ COOH \end{cases} \qquad \begin{cases} CN \\ CN. \end{cases}$$

Weddige originally obtained it from the former of these bodies; it has now been prepared from the latter.

The authors are still in doubt as to the position of the cyanogen in the cyanide of allyl alcohol.

W. A. T.

Diglycollamic Diuramide. By E. MULDER (Deut. Chem. Ges. Ber., v, 1011—1013).

BAEYER obtained hydantoin by the action of alcoholic ammonia on bromacetyl urea; and the author suggests that the action of alcoholic ammonia on β-bromopropionyl urea should lead to the formation of a substance, $CH_2.CH_2.CO.NH.CO.NH$, capable of being easily transformed into barbituric acid. But before attempting to form barbituric acid by this method, it was deemed advisable to study more accurately the action of alcoholic ammonia on bromacetyl urea. For this purpose the two substances were digested together in a water-bath, and the solid matter obtained on cooling was crystallised from water. Some analyses of this product gave results corresponding with hydantoin, and one analysis gave numbers agreeing with amido-acetyl urea. Other analyses indicated the reaction—

$$2(NH_2.CO.NH.CO.CH_2Br) + NH_3 = 2HBr + (NH_2.CO.NH.CO.CH_2)NH.$$

In order to verify this the crude product was dissolved in dilute hydrochloric acid, precipitated by ammonia, again dissolved in hydrochloric acid, and treated with platinum chloride. A platinum salt was thus obtained which crystallised in needles or prisms containing $2[(NH_2.CO.NH.CO.CH_2)_2NH.HCl].PtCl_4$. From this platinum salt the substance $(NH_2.CO.NH.CO.CH_2)_2NH$ was obtained in the free state. This product, diglycollamic-diuramide, is a colourless crystalline substance insoluble in alcohol and moderately soluble in hot water.

The residue obtained when the crude product is treated with dilute hydrochloric acid yielded, on crystallisation from water, a compound which appears to be triglycollamic triuramide $(NH_2.CO.NH.CO.CH_2)_3N$. The author intends to extend his investigation of this substance, and also to seek for amido-acetyl urea in the mother-liquors of the platinum-salt just mentioned.

T. B.

The Action of Potassium on Benzene, and of Ethyl Bromide on Naphthalene-potassium. By H. ABELJANZ (Deut. Chem. Ges. Ber., v, 1027).

WHEN benzene and potassium are heated together in a sealed tube to 240°—250°, they combine and form *benzene-potassium*. It is a black mass which appears blue when viewed in thin layers. In the dry state

it is very explosive, and it is decomposed violently by water. The gradual action of water on it gives rise to diphenyl.

When the compound of naphthalene and potassium described by Berthelot, is treated with ethyl bromide, a yellow hydrocarbon containing $C_{20}H_{12}$ is formed. (The author suggests that this may be dinaphthyl.)

T. B.

Crystalline forms of Dibenzyl and of Stilbene. By G. VOM RATH (Deut. Chem. Ges. Ber. v, 623).

BOTH these compounds form monoclinic crystals, the elements of which, denoting the clinodiagonal by a, the orthodiagonal by b, and the principal axis by c, are as follows:—

Ratio of Axes.

	a.		b.		c.	Angle ac.
Dibenzyl......	1·27026	:	1	:	1·91563	101° 32′·50″.
Stilbene......	2·1561	:	1	:	1·8549	113° 22′.

H. W.

On the alleged Synthesis of Terebene. By V. LOUGUININE (Deut. Chem. Ges. Ber., v, 930).

THE author finds that perfectly pure cymene (boiling at 172°—175° corr.) undergoes no alteration when its alcoholic solution is treated with sodium, or with an amalgam containing 3 per cent. of sodium, and hence infers that the cymene from which terebene has been said to be formed by reactions similar to those above mentioned, must have been prepared from cumin oil adulterated with oil of turpentine.

H. W.

Capability of Azobenzene to form Addition-products. By A. WERIGO (Ann. Chem. Pharm., clxv, 189—216).

Dibromazobenzene, $C_{12}H_8Br_2N_2$.—The author has investigated the nature of the brominated derivative of azobenzene obtained by him some time ago (*Ann. Chem. Pharm.*, cxxxv, 176), and finds it to be a substitution-product, dibromazobenzene, and not an addition-product, azobenzene dibromide. For, firstly, it possesses a remarkable stability, like azobenzene itself, and unlike the addition-products of this body; thus it can be distilled unchanged, and does not yield its bromine either to silver salts or to potassium hydrate, even when heated with the latter in sealed tubes. Secondly, fuming nitric acid converts azobenzene into trinitro-azoxybenzene (Petrieff, *Zeitschr. Chem.*, 1870, 264); and Sendzuk, who, at the suggestion of the author, has studied the action of fuming nitric acid upon the brominated body, finds that it produces,

besides the dinitro- and trinitro-products already described by the author, trinitrodibromo-azoxybenzene as the ultimate product. Thirdly, the brominated body yields hydrodibrom-azobenzene, analogous to hydrazobenzene, by the same method as that by which azobenzene yields the latter body. Fourthly, when digested with warm fuming sulphuric acid, it yields a sulpho-acid, $C_{12}H_8Br_2N_2SO_3,3H_2O$, the analogue of Griess's sulphazobenzolic acid. Fifthly, and most conclusively, the brominated body can be obtained by treating the alcoholic solution of monobromonitrobenzene with potassium hydrate, just as azobenzene is obtained from nitrobenzene.

Dibromazobenzene dissolves easily in boiling benzene, and separates from it on cooling in large yellow needles. It also dissolves readily in carbon sulphide and in chloroform. It melts at 205°, and sublimes without decomposition.

Trinitrodibrom-azoxybenzene, $C_{12}H_5Br_2(NO_2)_3N_2O$, is crystalline, and very difficultly soluble in alcohol; it melts at 174°, solidifying on cooling to a resinoid mass; at a higher temperature it decomposes.

Hydrodibrom-azobenzene, $C_{12}H_{10}Br_2N_2$.—On passing dry ammonia and hydrogen sulphide into an alcoholic solution of dibrom-azobenzene mixed with more of this substance undissolved, the excess of the dibrom-azobenzene gradually dissolves, and the solution soon becomes colourless. On adding water the hydrodibrom-azobenzene separates in fine, white, silky needles, readily soluble in alcohol and ether, and unaffected by exposure to the air. Like hydrazobenzene, it is decomposed in alcoholic solution by nitrous acid, yielding dibrom-azobenzene again, which separates in yellow crystals, thus:—

$$C_{12}H_{10}Br_2N_2 + O = C_{12}H_8Br_2N_2 + H_2O.$$

At 130° hydrodibrom-azobenzene becomes red, and melts; at 160° it begins to decompose. Heated to 150° and then cooled, it solidifies to a mass, from which hydrochloric acid removes monobromaniline, leaving dibrom-azobenzene. Its decomposition is, therefore, precisely analogous to that of hydrazobenzene:—

$$2C_{12}H_{10}Br_2N_2 = C_{12}H_8Br_2N_2 + 2C_6H_6BrN.$$

The author has not succeeded in converting it into a body analogous to benzidine.

Hydrodibrom-azobenzene appears to be trimorphous. Besides the silky crystals above mentioned, it can be obtained in white prisms which are at first transparent, but gradually become opaque in their alcoholic mother-liquor; in short, thick, yellow crystals; and in yellow laminæ. All the forms have the same melting point, and behave alike when heated.

Sulphodibrom-azobenzolic acid, $C_{12}H_8Br_2N_2SO_3,3H_2O$.—On digesting the warm solution of dibrom-azobenzene in fuming sulphuric acid for some time, and then pouring it into boiling water, the liquid becomes filled with the yellow crystals of the sulpho-acid, if a certain proportion of water has been taken. If more or less water than this be used the acid remains in solution. It thus resembles Griess's sulph-azobenzolic acid in being soluble both in water and in a sufficiently concentrated

sulphuric acid, as well as in the mode of its production. It is monobasic, readily soluble in water, alcohol, and ether—its solutions having an acid reaction. A concentrated hot aqueous solution gelatinizes when suddenly cooled, but gradually becomes filled with crystals.

It occurs in three forms, appearing under the microscope as very slightly coloured needles, broad yellow plates, and reddish crystals pointed at both ends. Its potassium salt resembles the free acid in appearance, but is less soluble in water, and still less so in alcohol. From its hot alcoholic solution it separates on cooling in orange-yellow needles. The silver salt is a yellow, amorphous powder, very little soluble in water or alcohol.

Dibrom-azoxybenzene, $C_{12}H_8Br_2N_2O$.—Sodium-amalgam, which converts nitrobenzene into azobenzene, does not convert monobromo-nitrobenzene into dibrom-azobenzene, but produces dibrom-azoxybenzene from it. This substance is yellow, crystalline, and readily soluble in hot alcohol and hot benzene. It melts at 175°.

Tetrabrom-azobenzene, $C_{12}H_6Br_4N_2$.—The analysis of this body, which is a bye-product in the preparation of dibrom-azobenzene, agrees well with the above formula. It is also obtained by allowing bromine to fall drop by drop into a hot, strong, alcoholic solution of azobenzene. It forms white crystals, very little soluble in alcohol, readily soluble in boiling benzene of high boiling point, from which on cooling it crystallises in white, silky needles. It is also but slightly soluble in chloroform, ether, and carbon sulphide. It melts at about 320°, and then begins to decompose and blacken. Strong nitric acid dissolves it, and the solution, when mixed with water, yields long yellow needles of a substance which explodes when heated. The author has obtained a body which appeared to be *tribrom-azobenzene*, but only once.

Reduction of Azoxybenzene to Azobenzene.—Phosphorus pentachloride acts readily upon melted azoxybenzene: the products of the action are phosphorus oxychloride and azobenzene. Alexejeff and Petrieff have shown that sodium-amalgam does not effect this reduction, but converts azoxy-compounds into hydrazo-products.

Addition-products of Azobenzene, (1.) $2C_{12}H_{10}N_2.3HBr$ and $2C_{12}H_{10}N_2.3HCl$ —The hydrobromide separates in the form of carmine-red crystals when dry hydrogen bromide is passed into a solution of azobenzene in carbon sulphide or chloroform. It very soon decomposes again on exposure into azobenzene and hydrogen bromide, and must be washed with carbon sulphide saturated with hydrogen bromide, in which it is only slightly soluble. It dissolves in pure carbon sulphide and in chloroform, being at the same time resolved into its proximate constituents. It is similarly decomposed by alcohol, ether, and water. Cautiously heated it yields azobenzene as a residue.

The hydrochloride is prepared in the same manner as the hydrobromide. It forms yellow crystals, and is still more unstable.

Like fuming solution of hydrogen chloride (Zinin), solutions of hydrogen bromide and hydrogen iodide convert azobenzene into the corresponding salts of benzidine.

In sealed tubes, a strong solution of hydrogen bromide begins to act upon azoxybenzene at 250°, the product of the action being dibromaniline hydrobromide. Solution of hydrogen iodide readily acts upon

azoxybenzene when heated with it, producing benzidine hydriodide and free iodine.

(2.) $C_{12}H_{10}N_2.HBr.Br_2$.—A body of this composition is obtainable in the three following ways:—(*a*) By adding excess of phosphorus pentabromide to a solution of azoxybenzene or of azobenzene in ether or in chloroform, and heating the mixture. The reaction proceeds quietly, hydrogen bromide is evolved, and the above addition-product, which must be washed, not with ether, but with carbon sulphide, crystallises out. Both carbon sulphide and ether decompose it, but the product of the decomposition is soluble in the former liquid, and so carried off by it. (*b*) By adding bromine to a solution of the body, $2C_{12}H_{10}N_2.3HBr$, in chloroform, and washing the crystals which separate with chloroform in which some bromine has been dissolved. (*c*) By adding bromine and then benzene to a solution of azobenzene in carbon sulphide, and exposing the mixture to sunshine, when the body in question separates in crystals which fill the liquid. The hydrogen bromide necessary for the formation of the body is generated by the action of the bromine upon the benzene; hence the use of exposing the mixture to sunlight.

It is a yellow, crystalline, very unstable compound, decomposed by ether, alcohol, carbon sulphide, and chloroform, but least of all by the last. From its hot concentrated solution in chloroform it can be partly recovered in crystals by rapid cooling. The presence of free bromine in these liquids diminishes their action upon it; and an excess of phosphorus pentabromide is essential in preparing it by the first of the above methods, in order to lessen the action of the ether. Azobenzene is always reproduced by its decomposition by these liquids, and the whole of the bromine is precipitable from its alcoholic solution by silver nitrate, silver oxide, or barium peroxide. Cautiously heated, it also yields azobenzene as a residue. Exposed to the air it slowly decomposes, with the same result. Over sulphuric acid under a bell glass it also yields azobenzene as the final product. But the body prepared by method (*c*), and usually by method (*a*), yields at first, during its exposure over the acid, ruby-red, short prismatic crystals, which increase in size for a time, and then themselves break up into azobenzene; while, when it is prepared by method (*b*), and occasionally by method (*a*), it does not yield these ruby-red crystals in its passage into azobenzene. The author, thinking that the two varieties might differ in composition by one being $C_{12}H_{10}N_2.2HBr.Br$, ascertained that this was not the case, by estimating with thiosulphate the amount of free bromine resulting from its decomposition, and finding it in both cases to be Br_2.

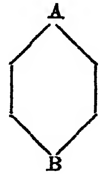
(3.) *Azobenzene hexbromide*, $C_{12}H_{10}N_2Br_6$.—On adding an excess of bromine to a dilute solution of azobenzene in chloroform kept cool, this substance crystallises out after some time in large, dark-red, transparent prisms which decompose with exceeding rapidity when removed from their mother-liquor. The author washed them with a solution of bromine in chloroform, and dried them in an atmosphere of bromine.

E. D.

Notes on Hydroquionone and analogous Substances. By O. Hesse (Deut. Chem. Ges. Ber., v, 1022—1027).

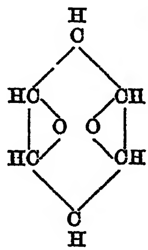
The researches of Stenhouse on pentachlororesorcin, and the fact

that tetrachloroquinone can readily fix two atoms of hydrogen which may be afterwards easily removed by oxidation, have convinced the author that hydroquinone and its isomerides (resorcin and pyrocatechin), do not contain hydroxyl. As two of these substances are often formed during the same reaction, we should expect to find a relation existing between them, which would allow one of them, when in the nascent state, to be easily transformed into another. These changes are explained by assuming that the molecule is constructed in accordance with the following scheme:—



A and B represent the poles of the molecule, and the line A B represents its axis. In accordance with this view, the molecule of hydroquinone, &c., is represented as follows:—

Resorcin.

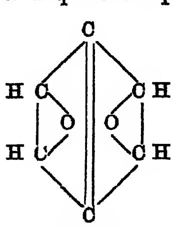


Hydroquinone.

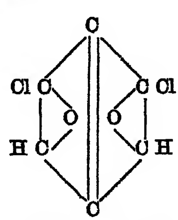
Pyrocatechin.

The changes occurring during the transformations above referred to, take place only at one pole of the molecule for one and the same substance. When both the polar hydrogen atoms coincide in polarity, hydroquinone is the result; but when they differ in polarity, resorcin or pyrocatechin is produced. If a change in the polarity of the hydrogen-atom situated at the pole A gives rise to pyrocatechin, a similar change in the polarity of the hydrogen-atom situated at the pole B will give rise to resorcin.

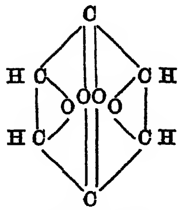
Quinone and some of its derivatives are represented by the following formulæ, which require no special explanation:—



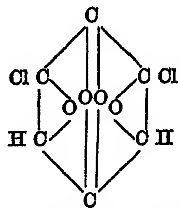
Quinone.



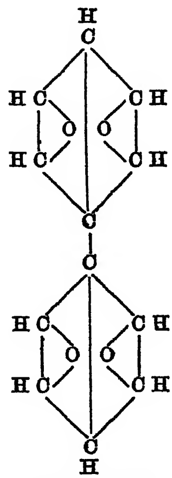
Dichloroquinone.



Quinonic acid
(not yet obtained),



Dichloroquinonic acid
(chloranilic acid).



Quinhydrone.

The author has investigated the discrepancies existing between the various accounts of hydroquinone, and concludes that there is only one form of this substance, that it melts at 172°—173° (uncor.) = 177·1°—177·5° cor., and crystallises from its solution in rhombic crystals.

T. B.

An Isomeride of Anthraquinone. By P. SCHÜTZENBERGER (Bull. Soc. Chim. [2], xvii, 2).

THE author, in repeating the experiments of Graebe and Liebermann, has observed the formation of an isomeric anthraquinone, which sublimes in beautiful red needles resembling alizarin, but differs from that body by its insolubility in potash and in ammonia. On heating its vapour to 300°, it is converted into yellow anthraquinone.

H. W.

Formation of Nitro-derivatives of Anthraquinone. By RUD. BOETTGER and THEODOR PETERSEN (Deut. Chem. Ges. Ber., vi, 20).

THE authors have succeeded in converting anthraquinone into α-dinitroanthraquinone by the direct action of nitric acid alone. This is effected by boiling anthraquinone with red fuming nitric acid of sp. gr. 1·52 for some hours. Nitric acid of lower sp. gr. than 1·44 scarcely attacks anthraquinone dissolved in it, even on prolonged boiling.

J. R.

Nitrogen-compounds of Anthraquinone. By RUD. BOETTGER and THEODOR PETERSEN (J. pr. Chem. [2], vi, 367—373).

α-Mononitroanthraquinone, $C_{14}H_7(NO_2)O_2$.—The authors have previously shown that anthraquinone is easily converted into dinitroanthraquinone by the action of a mixture of strong nitric and sulphuric acids. They have now succeeded in replacing *one* of the atoms of hydrogen in anthraquinone by the group NO_2, by the direct action of nitric acid. Their process is as follows:—Anthraquinone is dissolved in six to twelve times its weight of warm nitric acid, of sp. gr. 1·5, and the solution is boiled for half an hour or longer. The liquid is then agitated with a large quantity of cold water, and the pale-yellow flocks thereby thrown down are washed with cold water. The product is a pale-yellow electric powder, subliming readily in delicate needles, which melt at 230°. It is insoluble in water, very sparingly soluble in ether and alcohol, more freely in ethyl acetate, benzene, chloroform, turpentine, and glacial acetic acid, from which last it crystallises beautifully. It is easily soluble in nitrobenzene, in strong sulphuric acid, and in aniline (which is an excellent solvent for anthraquinone and anthracene-compounds generally), forming with the last a resinous compound, which dissolves with fine fuchsine-red colour in acetic acid, ethyl acetate, and other ethereal solvents. A mixture of strong nitric and sulphuric acids converts it into dinitroanthroquinone. Its behaviour with fused alkalis is remarkable, *alizarin being formed in abundance*, together with a certain quantity of anthraquinone.

α-Monoamidoanthraquinone, $C_{14}H_7(NH_2)O_2$.—This body is easily obtained by the action of reducing agents upon the preceding compound. The authors prepare it preferably by boiling mononitroanthraquinone in fine powder with a moderately strong solution of sodium sulphydrate for some time, diluting with water, cooling, filtering, and washing the product with cold water. Thus prepared, it forms a bright brick-red powder, which sublimes easily in small needles. Melting point 256°. It resembles the foregoing compound in solubility. It does not appear to combine with acids.

α-Diazoanthraquinone nitrate, $C_{14}H_7N_2O_2.NO_3$.—A body having this composition is thrown down in the form of a pale-red powder, when a current of nitrogen tetroxide is passed into a solution of the amide in ether-alcohol. It is sparingly soluble in water, freely in ethyl acetate and alcohol, insoluble in ether. When warmed with water, it evolves

nitrogen abundantly, deposits flocks, and afterwards contains free nitric acid. These flocks yield on heating a sublimate of glistening yellow crystals, which exhibit the properties of Graebe and Liebermann's oxyanthraquinone, and melt at 202°.

$$C_{14}H_7O_2.N_2.NO_3 + H_2O = C_{14}H_7O_2.OH + N_2 + NHO_3.$$

α-Mononitroanthraquinone, heated to 200° with twelve times its weight of strong sulphuric acid, evolves a large quantity of sulphur dioxide. On afterwards pouring the solution into cold water, it deposits fine violet-red flocks of a body which the authors regard as *imidohydroxyl-anthraquinone*, $C_{14}H_6O_2\left\{\begin{matrix} N\overset{II}{=}N \\ OHOH \end{matrix}\right\}C_{14}H_6O_2$.

After purification it forms a blood-red powder, which melts to a dark cherry-red liquid, and yields a sublimate of rose-red needles, melting at 240°. In solubility it resembles the preceding compounds.

The authors are continuing their investigation of the nitrogen-compounds of anthraquinone.

J. R.

Dibenzyl-dicarbonic Acid. By A. Franchimont (Deut. Chem. Ges. Ber., v, 1048—1050).

The author has been endeavouring to obtain an acid of the formula $C_6H_5{-}CH\begin{matrix}\diagup CO.OH \\ \diagdown CO.OH\end{matrix}$ which may be regarded as phenylmalonic acid. Although unsuccessful in this, he has been led to other results.

By action of phosphorus pentachloride on bitter almond oil, benzylene chloride is obtained, and this, heated with pure potassium cyanide, should yield a cyanide of the formula $C_6H_5.CH(CN)_2$, which, by the action of potash or of hydrochloric acid, ought to furnish the corresponding acid. A brown viscid mass, however, is obtained which, on treatment with potash or hydrochloric acid, yields only benzoic acid.

The author then took phenylacetic acid as starting-point, and, acting upon it with bromine with the aid of heat, obtained phenyl-bromacetic acid, from which, by treatment with alcohol and hydrochloric acid gas, the ethyl ether was prepared. This ether, heated in sealed tubes with alcoholic solution of potassium cyanide, gave potassium bromide and a slightly coloured solution, which was boiled with potash. Much ammonia was evolved, and after protracted heating, the solution was evaporated to dryness, and supersaturated with hydrochloric acid. A mixture of gases, smelling of hydrocyanic acid, was evolved and an acid precipitated, which was crystallised from boiling water and then from hydrochhloric acid, in which it is much more soluble. Analysis of the acid and of its barium and silver salts led to the formula

$$\begin{matrix} C_6H_5.CH.CO.OH \\ | \\ C_6H_5.CH.CO.OH. \end{matrix}$$

This was confirmed by the preparation of the mono-ethylic ether, and by heating with lime, when the two hydrocarbons, dibenzyl and stilbene, were obtained, the latter resulting from the action of heat on the former.

Dibenzyl-dicarbonic acid is closely connected with the dibenzyl-carbonic acid,

$$\begin{array}{l} C_6H_5.CH.CO.OH \\ \quad | \\ C_6H_5.CH_2 \end{array}$$

discovered by Wurtz.

It crystallises from diluted hydrochloric acid with a molecule of water, from benzene in shining crystals, which soon become dull. The first melt at 182°, then become solid, and melt again at 222°. The latter melt first at 169°—170°, then solidify, and melt a second time, when the temperature reaches 222°. Probably the acid crystallises in combination with benzene. The monethylic ether crystallises from ether and melts at 140°.

An experiment made with the hope of obtaining the same acid from the ether of phenyl-bromacetic acid by potassium monosulphide, gave a beautifully crystalline sulphuretted body, which was decomposed by water, and is probably represented by the formula—

$$\begin{array}{c} C_6H_5—CH—COOH \\ | \\ S \\ | \\ C_6H_5—CH—COOH. \end{array}$$

W. A. T.

The Reduction of Mononitro-naphthoic Acid

By P. v. Rakowski (Deut. Chem. Ges. Ber., v, 1020—1022).

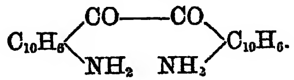
The isomeric naphthoic acids were prepared by the method of Merz, and it was found that the naphthoamide simultaneously formed may be converted into naphthoic acid by renewed treatment with potash. The isomeric acids thus produced were separated by taking advantage of the slight solubility of the β-calcium salt. The nitration of β-naphthoic acid was effected by boiling it with nitric acid (sp. gr. 1·2) until red fumes were no longer evolved.

When β-nitro-naphthoic acid was treated with tin and hydrochloric acid, a violent action took place. The product was boiled with ammonia carbonate and filtered, the substance deposited on cooling being then crystallised from weak alcohol. Analysis led to the formula—$C_{11}H_8NO$ or $C_{22}H_{16}N_2O_2$.

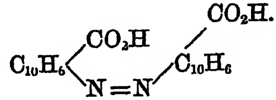
The new substance does not combine either with acids or with bases, and is not precipitated from its solution in hot water by the addition of metallic salts.

It is scarcely soluble in cold water, but is more soluble in that solvent when hot, and is deposited on cooling in microscopic flexible needles. Ether and alcohol dissolve it readily, and the latter fluid deposits it in tolerably long prisms. It melts at 174°, solidifies at 155,° and begins to sublime in small needles at 125°. Concentrated sulphuric acid dissolves it, and it is precipitated from the solution on the addition of water. When potassium bichromate is added to its solution in sulphuric acid, the liquid becomes dark blue, and the addition of water causes the separation of violet flocks.

The author gives the following constitutional formula for the new substance:—



It may also be obtained by the action of iron and acetic acid on β-mononitronaphthoic acid. The action of ammonium sulphide on this acid did not give rise to the amido-compound, but a small quantity of a product was obtained, which on analysis gave numbers corresponding to azo-naphthoic acid—



T. B.

On Phthalyl, the Radical of Phthalic Acid. By EMILE ADOR (Ann. Chim. Phys. [4], xxvi, 417—426).

Phthalyl Chloride, $C_8H_4O_2Cl_2$, is obtained by gently boiling 1 mol. of phthalic acid with 2 mols. phosphorus pentachloride for four or five days: the addition of phosphorus oxychloride facilitates the reaction. As soon as the disengagement of hydrochloric acid has ceased, the oxychloride is distilled off, the temperature then raised to 190°, and carbonic anhydride passed through the liquid to drive out the last traces of the pentachloride. Phthalyl chloride is a light yellow liquid, heavier than water, which decomposes it slowly with formation of phthalic acid. It boils without decomposition at 270°.

Phthalyl, $C_{16}H_8O_4$.—Finely divided silver, dried at 150°, is dropped gradually into phthalyl chloride, in the proportion of 14 grams of the former to 10 of the latter. A brisk reaction ensues, which is finished by heating the mixture to 150° for some hours. The whole is then treated with boiling water, and the dried residue exhausted with alcohol. The insoluble portion is heated in a combustion-tube in a gentle current of carbonic anhydride, when the phthalyl sublimes as an orange-yellow mass, which is treated with hot water, and recrystallised from boiling phenol The yield was 18·4 per cent.; theory requires 65 per cent.

Phthalyl is insoluble in water, and almost insoluble in alcohol, ether, chloroform, carbon sulphide, and hydrocarbons. It dissolves in hot phenol, and in cold concentrated sulphuric acid. From its solution in phenol it is precipitated by alcohol. It melts above 300°, sublimes, and distills; oxidises when heated in the air.

Diphthalic Aldehyde, $C_{16}H_{10}O_5$.—Alkalies in the cold have no action on phthalyl. When, however, phthalyl is boiled with a dilute solution of soda, a salt is obtained from which hydrochloric acid precipitates a bulky yellowish acid, insoluble in water. This acid is also formed by the action of sodium on phthalyl suspended in alcohol. This acid is but little soluble in alcohol, ether, chloroform, and hydrocarbons. It is soluble in hot phenol, in the alkalies, and their carbonates. It melts above 300°, splitting up into phthalyl, phthalic acid and a new acid. When dried, it forms a light white non-crystalline powder. It dissolves

in ammonia, and the solution when heated on the water-bath deposits phthalyl. The neutral filtrate reduces silver nitrate, whence it seems to follow that this acid is really an acid aldehyde produced from phthalyl by simple addition of water—

$$C_{16}H_8O_4 + H_2O = C_{16}H_{10}O_5 = C_6H_4\left\{\begin{matrix} COOH & COH \\ CO\text{———} & CO \end{matrix}\right\}C_6H_4.$$

Phthalyl heated with concentrated potash forms first the acid aldehyde of diphthalic acid, then diphthalic acid, and finally on fusion, phthalic acid. Nitric acid transforms the aldehyde into diphthalic acid.

Diphthalic Acid, $C_{16}H_{10}O_6$, is obtained from phthalyl by the prolonged action of alkalis, aided by heat and exposure to air, or by the action of nitric acid. Manganese dioxide and sulphuric acid can also be employed, but the reaction is then slow and imperfect. Diphthalic acid is a crystalline powder; almost insoluble in water, alcohol, and ether, sparingly soluble in hydrocarbons, chloroform, and carbon sulphide, easily soluble in phenol, from which solution it crystallises in fine yellowish needles. It melts at 265°, effervesces, and yields a sublimate of anhydrous phthalic acid (melting at 127°) phthalyl also being simultaneously formed. The silver, sodium, barium, copper, and lead-salts were prepared.

Strong sulphuric acid dissolves diphthalic acid: the solution heated for a short time and thrown into water, yields diphthalic anhydride. The latter melts at 228°, and slowly reproduces the acid if heated with water or soda-solution. Bromine dissolves diphthalic acid in the cold without change.

Dichlorophthalyl, $C_{16}H_6Cl_2O_4$.—Phthalyl heated in a sealed tube for five hours to 160° with 2 molecules of phosphorus pentachloride PCl_5, forms a clear brown liquid together with white crystals. These crystals were insoluble in water, scarcely soluble in alcohol, somewhat soluble in benzine, from which solution hexagonal tables crystallised out, melting at 248°, solidifying at 196°, and remelting at 233°. The body could be distilled colourless, and the distillate crystallised on cooling. Concentrated sodium hydrate resinised it. Analysis gave the formula, $C_8H_3ClO_2$. Hot concentrated alcoholic potash dissolved this body; from the solution acids precipitated a new acid in microscopic hexagonal tables, containing no chlorine, soluble in alcohol and benzene, insoluble in water, melting, blackening, and subliming at 250°. By acting on phthalyl with bromine in sealed tubes, a compound, $C_{16}H_7BrO_4$, was obtained. Phthalyl dissolves in cold sulphuric acid, and is precipitated on dilution. If, however, it be heated, it is decomposed, and on neutralising with baryta, treating with carbon dioxide, and evaporating to dryness, it gives a reddish brown salt, very soluble in water, and having the composition, $C_{16}H_6O_4Ba.2SO_3$. The free acid could not be obtained in the crystallised state.

A resinous product was obtained by treating with alcohol the products of the action of silver on dichlorophthalic acid. It melts below 100°, and is almost insoluble in water. When treated with sodium carbonate, it leaves impure phthalyl, and a resin soluble in alcohol, and precipitated by water. The sodium carbonate solution treated with hydrochloric acid, gave diphthalic acid and a small quantity of a resinous acid.

C. G. S.

Physiological Chemistry.

The Carbohydrates, and the mode in which they are Digested and Absorbed. By E. Brücke (Wien. Acad. Ber., lxv, [3], pp. 126—161).

I. *Starch, Dextrin, and Glycogen.*—The author first discusses the properties of what has been described as dextrin. The substance called dextrin by Biot became blue with iodine. Béchamp described as dextrin a substance which did not become so coloured, and attributed the reaction of Biot's dextrin to admixture with soluble starch. Nasse shows that the violet or red tint which dextrin is said in most text books to give with iodine, is a mixture of a blue depending on soluble starch (amidulin), and of a red due to dextrin proper. Béchamp's dextrin, which does not become coloured, he calls *dextrinogen.* Brücke agrees with Nasse in this respect. In order to avoid confusion with regard to these various substances, he proposes the name *achrodextrin* for Nasse's dextrinogen, and the term *erythrodextrin* for Nasse's dextrin, the substance which is coloured red by iodine. Neither erythrodextrin nor achrodextrin reduces copper solution; when they do so, it is owing to refracting. The reduction of copper by commercial dextrin is dependent on the presence of sugar. Griesmayer, whose dextrin I corresponds to achrodextrin, and whose dextrin II is the same as erythrodextrin, states that the latter has a greater affinity for iodine than starch. Brücke does not agree with this, for he finds that the blue colour of the starch appears before the red of the erythrodextrin, when the two are present together, at ordinary temperature (18° C.), though at higher temperatures the affinity of the two great substances seems to be equal.

Dextrin may be separated from starch by Griesmayer's method (modified), viz., precipitation of the starch by means of tannin; but in order to separate the two substances, erythrodextrin and achrodextrin, from each other, the best method, according to Brücke, is to fractionate with alcohol. First the starch is precipitated, if it has not been previously removed by the tannin, then the erythrodextrin, and lastly the achrodextrin, which generally carries with it a greater or lesser proportion of sugar.

A part of the achrodextrin is also carried down with the erythrodextrin, and therefore in small quantities, such as occur in digestion experiments, it is impossible to arrive at perfectly accurate quantitative results.

Various other reagents for starch and dextrin are given, but for these reference must be had to the original.

The products of the conversion of starch differ according to the method employed. The ordinary commercial dextrin made by simply roasting raw starch is a mixture of soluble starch and true dextrin. That made according to Payen's method (viz., moistening with nitric acid, drying, and roasting) contains, along with erythrodextrin, both achrodextrin and sugar. When starch is digested with dilute sul-

phuric acid, at first amidulin is formed, then erythrodextrin, and this passes after longer digestion into achrodextrin and sugar. The action of infusion of malt on starch is different. When the digestion has gone on for some time, a substance is formed which resembles erythrodextrin in being coloured red by iodine, but differs from it, among other things, in being completely precipitated by tannin.

Brücke calls this substance *erythamylum*. This substance has a greater affinity for iodine than starch has, so that when the two are together, the red reaction shows itself before the blue.

The reaction, however, may be observed even in fresh starch-paste before the action of a ferment. It would appear that the erythamylum is not a product of the conversion of starch, but rather the remains of the starch granules, closely united with Nagele's cellulose, and resisting the action of ferments longer than the granulose itself.

The further action of malting is to cause a disappearance of this substance with or without a residue. This residue, when present, occurs in the form of a slimy deposit, which becomes coloured red by iodine, while the supernatant fluid remains uncoloured.

Erythrodextrin seems also to be formed, but is rapidly destroyed by the further action of the ferment; but the fluid still contains considerable quantities of achrodextrin, and the process of malting seems to be the best adapted for producing achrodextrin in quantity. Diastase acts little or not at all on achrodextrin, while it acts on erythrodextrin as energetically as on starch itself. Glycogen in many respects resembles erythrodextrin in its reactions, but it differs from it in forming opalescent and never clear solutions.

II. *Digestion of Boiled Starch.*—The changes which starch undergoes in the stomach were studied in dogs which were killed from one to five hours after being fed on a meal principally composed of starch. The contents of the stomach and duodenum were separately analysed.

In the stomach along with a greater or lesser quantity of unaltered starch-mucilage, according to the extent to which digestion had proceeded, large quantities of soluble starch and erythrodextrin were found; the latter especially towards the end of gastric digestion. Achrodextrin is also formed in the stomach, but apparently only in very small amount. Sugar, unless it has been given with the food, is either not found in the stomach, or if so, only in very small quantity. In the small intestine sugar was always found, whether it had been given in the food or not.

Erythrodextrin is not found, or if so, the quantity is almost inappreciable. In reference to these results, it is instructive to note in the first place that even after a meal of starch, only traces of sugar are found in the stomach, notwithstanding that in the mouth the starch comes in contact with the saliva, and also in the stomach with the saliva which is constantly being swallowed. The cause of this is to be ascribed to the influence which the acid of the gastric juice exerts in checking the diastatic action of the saliva. In the second place, the occurrence of such large quantities of soluble starch and erythrodextrin in the stomach requires explanation. The formation of the soluble starch appears to be due to the action of the acid on the gastric juice, which thus acts on starch like other acid solutions. The formation of

erythrodextrin is more difficult to understand, because the amount of acid normally existing in the gastric juice is not sufficient at the ordinary temperature of the body to convert starch into this substance. After careful investigation, it appeared that part at least of the erythrodextrin may have been formed by the *successive* action of saliva and acid on the starch. Though the conditions for this successive action exist during the processes of mastication and gastric digestion, yet the quantity found could hardly be attributed to this source alone.

An elaborate series of investigations led Brucke to suppose that the production of the chief part of the erythrodextrin is due to lactic acid formation, which he regards as a normal factor in the digestion of starch and sugar in the stomach. This fermentation is entirely independent of the saliva and the gastric juice, and takes place in the stomach under the same conditions as it does outside the body. Starch-mucilage will undergo the lactic acid fermentation and produce dextrin and sugar, without the aid of anything but some ferment existing in the starch itself, or gaining access to it from without. The lactic acid fermentation in the starch does not usually result in the formation of a large amount of acid, but would do so if longer time were allowed. The concomitant formation of dextrin seems to point to the fermentation process as a normal preparation of the starch for more rapid transformation into sugar in the duodenum under the influence of the pancreatic juice. Only sugar and achrodextrin are found in the small intestine. The pancreatic secretion has some influence in changing achrodextrin into sugar, but part of the process is without doubt the continuation of the fermentation. The intestinal juice does not seem to have much influence on the formation of sugar in the small intestines.

D. F.

On the Quantity of Carbonic Acid Excreted by the Human Skin. By H. AUBERT (Pflüger's Archiv. f. Physiologie, Bd. iii, Heft 11, pp. 539—552).

VERY various estimates have been made of the quantity of carbonic acid excreted by the skin, the differences depending to a great extent on the methods of calculation adopted by different experimenters.

Gerlach estimates the amount at from 8—9 grams in the 24 hours; Reinhard gives it as 2·23 grams on an average; while Scharling states the amount at 32 grams. In order to determine the amount with more accuracy, Aubert, instead of calculating the quantity excreted by the whole surface from that evolved in a given time from a restricted portion of the skin, adopts the method of enclosing the whole body, with the exception of the head, in an air-tight chamber, through which ventilation can be effected by means of a measured current of air free from carbonic acid. The air of the perspiration chamber is drawn through bulbs (Schulze's) filled with titrated solutions of caustic baryta for the purpose of absorbing the carbonic acid. The minute details of the apparatus must be read in the original. Each experiment lasted for a period of two hours.

After the necessary corrections have been made for the carbonic acid

remaining in the chamber, it was found that, as the mean result of several observations, the maximum quantity of carbonic acid given off by the skin, in the 24 hours was 6·3 grams; the minimum was 2·3 grams, and the average 3·87 grams.

When the quantity excreted by the head is approximately determined, the whole quantity is estimated at 4 grams of carbonic acid in the 24 hours.

This quantity, however, must not be regarded as constant, for it is liable to variations under different bodily conditions, such as exercise and, to a great extent, on temperature. The influence of temperature in increasing the carbonic acid is seen in the experiments. It is probably due to the increased cutaneous circulation.

When compared with the amount of carbonic acid given off by the lungs (c. 900 grams), the quantity given off by the skin will be seen to be comparatively insignificant, and little error will be committed if the quantity of carbonic acid in the exposed air be taken to represent the carbon excretion of the body.

Experiments were also made with limited surfaces of the body, such as the hand. The results show that such determinations cannot be applied to the whole surface, as all parts of the body do not excrete carbonic acid in the same proportion. This explains many of the differences in the estimates of previous observers.

D. F.

On the Expulsion of Carbonic Oxide and Nitric Oxide from Blood. By S. Podolinski (Pflüger's Archiv. f. Physiologie, Bd. vi, Heft 11, pp. 553—555).

Donders recently showed (see this Journal, March, 1872, p. 253) that carbonic oxide may be expelled from blood by indifferent gases, and Zuntz (*Chem. Soc. J.*, 1872, p. 899) has succeeded in separating it by means of the Torricellian vacuum. Podolinski, under the direction of Hermann, makes further researches on this subject, and extends them to nitric oxide. He finds that when small quantities of blood saturated with carbonic oxide are thoroughly mixed with hydrogen, the carbonic oxide is thoroughly expelled in the course of half an hour. Oxygen acts more rapidly. In regard to blood containing nitric oxide, hydrogen also expels the nitric oxide, but less rapidly than in the case of carbonic oxide. Hydrogen alone was experimented with in order to avoid the formation of nitric peroxide. Hence the nitric oxide compound of hæmoglobin, as well as the carbonic oxide compound, stands in the same category as oxyhæmoglobin. The order of stability is the oxygen, carbonic oxide, and nitric oxide hæmoglobin. Each can be expelled by the one immediately following, and each also more easily expelled by the one immediately preceding that by any other indifferent gas.

D. F.

New Experiments on Respiratory Combustion. Oxidation of Sugar in the Arterial System. By A. ESTOR and C. ST. PIERRE (Compt. rend., lxxvi, 54).

BY injecting a solution of glucose into the femoral vein of a dog, and immediately examining blood from the femoral artery on the other side, the authors find that the glucose is rapidly destroyed, and that during its presence the oxygen disappears. As the result of their experiments, they consider that respiratory combustion occurs in the arteries.

W. A. T.

Distribution of Iron in the Constituents of the Blood. By BOUSSINGAULT (Compt. rend., lxxv, 229).

100 parts of dry fibrin were found to contain 0·0466 iron; the dried corpuscles, 0·350; the dried albumin, 0·0863. The corpuscles, therefore, contain seven times as much iron as the fibrin, and four times as much as the albumin.

H. W.

Contribution to the knowledge of Hæmoglobin. By E. RAY LANKESTER (Proc. Roy. Soc., xxi, 78).

RELATES to the spectroscopic detection of hæmoglobin, and its occurrence in animal organisms. The chief results have already been given in this Journal (p. 255 of last volume).

H. W.

Physiological Action of Quinic Acid and Ferric Chloride. By RABUTEAU (Compt. rend., lxxv, 219).

QUINIC acid, like nearly all vegetable acids, is burnt in the organism and exerts no physiological action. Its alkali-salts are thereby converted into bicarbonates, which render the urine alkaline if they are taken in sufficient doses, *e.g.*, 5—6 grams in a day.

Ferric chloride, as the author has previously shown, is reduced by contact with proteids and various other organic substances, and undergoes a like change in the organism.

H. W.

Behaviour of Potassium Iodate in the Animal Organism. By F. MELSENS (Ann. Chim. Phys. [4], xxv, 157).

THE iodate is reduced in the organism, and converted into iodide. The iodide itself is harmless, but the iodate is an actual poison.

H. W.

A new kind of Calculus from Oxen—Magnesium Lithurate. By G. ROSTER (Ann. Chem. Pharm., clxv, 104—107).

A VETERINARY surgeon at Pietrasanta in Tuscany, noticed that the oxen employed in agricultural operations in the neighbourhood, from time

to time passed calculi with their urine. These were submitted to the author for examination. He has not been able to obtain any precise information with regard to the circumstances under which they are formed, but has only ascertained that they are noticed in the case of heavily worked beasts, which are chiefly fed on the juicy stems of the maize-plant. The largest stone weighed 1·02 grams, the smallest ·15 gram; they are light, although they do not float on water, and are usually pale straw-yellow in colour, though sometimes they occur of a greyer tinge. They cannot be crushed between the fingers, but are easily pulverised in a mortar; under the microscope long transparent prisms are distinguishable in the powder.

It is found that the calculi consist of the magnesium salt of a nitrogenous acid, together with traces of calcium carbonate and slimy matter. This salt is readily purified by repeated recrystallisation from boiling water.

Boiling water dissolves a considerable quantity of the pulverised substance, from which it separates on cooling in the form of a crystalline snow-white, glistening precipitate, consisting of transparent monoclinic prisms truncated by two planes at either end, and fine needles. Concordant determinations of the various elements in different samples lead to the formula $C_{29}H_{36}N_2MgO_{17}$, or $C_{30}H_{36}N_2MgO_{18}$; on the whole the values found agree somewhat better with the former.*

On adding hydrochloric acid to a warm saturated solution of the magnesium salt and allowing it to stand, fine snow-white needles of an acid melting at 200° separated; after recrystallisation from boiling water, in which the acid is moderately soluble, the melting point became 205°, but it was not raised beyond this by further recrystallisation. This acid the author terms *lithuric acid.*

H. E. A.

Spontaneous Alcoholic and Acetic Fermentation of the Liver, and Physiological Alcohol in Human Urine. By A. Béchamp (Compt. rend., lxxv, 1830).

The entire liver of an animal just killed, when washed with distilled water and immersed in creosoted water contained in a vessel from which all air has been expelled by a current of carbon dioxide gas, soon begins to disengage carbon dioxide, hydrogen, and a little hydrogen sulphide. In three or four days, the liver and the water in which it has been lying, are found to have become very acid without having acquired any putrefactive odour. On examination, notable quantities of alcohol and acetic acid can be detected, besides another acid which appears to be lactic acid.

The author has previously shown that a similar change occurs within eggs, the contents of which have been broken down by violent

				Mean of analyses.
* C_{29}........	49·15	C_{30}........	48·91	49·13
H_{36}	5·09	H_{36}	4·89	5·02
N_2........	3·95	N_2........	3·81	3·70
Mg	3·39	Mg........	3·26	3·58
O_{17}........	38·12	O_{18}........	39·13	38·57

shaking. The albuminoïd matters in either instance take but little or no part in the phenomenon, while the glucose and glycogenic matters present disappear. The author attributes the fermentation to the action of the microzymas of the liver and of the yolk of egg, and the organic forms evolved from them. In the above experiment, the microzymas become, for the most part, evolved into bacteria, but the microzymas are themselves active.

There appears, therefore, no reason why alcoholic fermentation may not occur in the liver of a living animal, and the author has, consequently, sought for alcohol in the urine. This he has found in sufficient quantity to identify it by inflaming it, in the urine of elderly persons not making use of alcoholic drinks. The urine of younger persons does not yield equally decided results. E. D.

Antiseptic Properties and Physiological Action of Sodium Silicate. By A. RABUTEAU and F. PAPILLON (Compt. rend., lxxv, 1030).

FURTHER experiments have confirmed the results previously announced (an abstract of which has appeared in this Journal, vol. xi, 85), except that in certain cases the antiseptic effect of the salt is temporary.

Action upon Blood.—Fresh blood, to which had been added 1 per cent. of sodium silicate, remained inodorous and free from vibrios and bacteria for eight days; after that time a feeble odour of decomposition became perceptible. The globules of the blood were completely dissolved in about an hour after the addition of the silicate.

Action upon Pus.—One per cent. of salt added to pus which had been obtained five days before from a purulent pleurisy, and was exhaling a disagreeable odour, stopped the decomposition; it became inodorous and remained so at the end of six days. The globules were not dissolved, but in a second experiment with a larger proportion of the salt, the solution was complete.

Action upon Bile.—Fresh ox bile, with 1 per cent. of the salt, showed no sign of decomposition at the end of ten days.

Action upon Egg.—An egg beaten up with 1 gram of the silicate presented no trace of putridity at the end of twenty days.

Action upon the Sinapinic Fermentation.—One of Rigollot's sinapine plaisters, dipped in a dilute solution of the salt, produce no rubefaction of the skin. When the rubefaction has been produced by one of the ordinary plaisters, the silicate will cause the pain and the redness to disappear.

J. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of the Spectrum Colours on the Decomposition of Carbon Dioxide by Plants. By W. PFEFFER (Pogg. Ann., cxlviii, 86—99).

THESE experiments have been already given (*Versuchs-Stat. Organ.*, x, 356; *Chem. Soc J.* [2], x, 1107). The author remarks that Müller

does not give sufficient details of his experiments to allow of a full criticism, but that the small quantity of carbon dioxide decomposed was evidently prejudicial to the results. Lommel's later experiments (*Pogg. Ann.*, cxlv, 442), only show that more growth takes place under the influence of the middle red rays than under that of the outer red rays.

E. K.

The part borne by Chlorophyll in the Assimilative Action of Plants and the Spectrum of Leaves. By E. GERLAND (Pogg. Ann., cxlviii, 99—115).

THE author suggests that chlorophyll is the product rather than the producer of assimilation, which is more probably due to the protoplasmic granules with which the colouring matter is associated.

Young plants of *Scrophularia nodosa* and *Phaseolus multiflorus* grown in the light, transmitted through a strong alcoholic solution of chlorophyll, flourished better than similar plants grown in total darkness; at the end of the experiment, which lasted nine days, the solution, though unchanged in colour, was slightly modified, as shown by the almost total disappearance of Band III. Comparisons of the spectrum of alcoholic solution of chlorophyll at different temperatures, and of alcoholic and ethereal solutions alone and mixed with water, glycerin, and soap-water, did not fully confirm the view of Kraus (*Botanische Zeitung*, 1872), that the displacement of the dark bands is caused by the difference in density of the solvent of the chlorophyll, and that the greater the density the greater is the displacement which takes place towards the red end of the spectrum.

Though in some cases, as in Feussner's experiments (*Monatsber. d. Akad. d. Wissensch. in Berlin*, 1865), with saline solutions at different temperatures, an apparent displacement of the bright bands occurs, yet the dark bands, measured from their point of maximum intensity, are not displaced; no light, therefore, is thrown by these experiments on the cause of the displacement of the dark bands in the spectrum of leaves. The mixture of water, glycerin, or soap-water with an alcoholic solution of chlorophyll, causes the cessation of fluorescence, but the purely mechanical mixture of these substances with an ethereal solution produces no such action.

E. K.

Effect of Coal-gas upon Trees and Shrubs. (Dingl. Polyt. J., ccvi, 345).

A SERIES of experiments was tried in Berlin in order to determine the amount of damage done to the roots of trees and shrubs by gas escaping from pipes through the soil, and thus coming in contact with them. It was found that even so small a quantity of coal-gas as 25 cubic feet per diem, distributed in 144 square feet of ground, and at 4 feet deep, *i.e.*, through 576 cubic feet of earth, killed in a short time the rootlets of trees of every kind which came in contact with it, and that this damage was sooner done, the firmer and closer the surface of the ground above.

W S

Chemical Researches on the Ripening of Grapes. By E. POLLACCI (Gazzetta Chimica Italiana, ii, 392—394).

THE author has proved, by a comparison of the amount of sugar and of acid in the external and internal portions of the flesh of the fruit, that the part nearest the centre contains more of the acid principle, and is, consequently, the last to ripen. During the ripening, the amount of sugar goes on increasing to a certain point, and then remains stationary, whilst the proportion of acid still continues to decrease, so that the grape must be considered to be ripe, not, as heretofore, when the amount of sugar ceases to increase, but rather when the acidity no longer diminishes.

The paper is accompanied by a table of the results obtained with Aleatico, Procanico, and white Muscatel grapes, gathered during the months of August, September, and October.

C. E. G.

On the Composition of the Seeds of Two Varieties of Cane. By A. COSSA (Gazzetta Chimica Italiana, ii, 373—379).

AT the time of cutting a large crop of sugar-canes at Chivasso, in Piedmont, it was found that about half of them did not yield any sugar, the plants having all the characters of the common cane. This evidently depended on the quality of the seeds sown, which, on examination, proved to be of two kinds. Of these the sugar-yielding variety is of a shining black, whilst the others have a reddish shade, the latter also weigh more, germinate more easily, and contain less water, fatty substance, and nitrogen than the former, but the ash of the husks contains more silica. These two varieties of seeds were from successive reproductions of the plants, and it would seem that hybridization with the common cane is one great cause of the deterioration. The author concludes by suggesting that this deterioration, and the ready alterability of the canes when cut, render the cultivation of the beet-root far more advantageous than that of the sugar-cane.

C. E. G.

Composition of the Ash of the Leaves and Fruit of the Lemon Tree. By A. COSSA (Gazzetta Chimica Italiana, ii, 385—392).

THE author, after stating that the only article in relation to this subject which he has been able to discover, is an analysis of the ash of lemon seeds by Souchay, proceeds to detail the results of his examination of the fruit and leaves of the lemon grown in Sicily. He gives the percentage of water, organic matter, and inorganic matter in the leaves, and a complete analysis of their ash; also the amount of rind, parenchyma, seed, and juice contained in the fruit, analyses of the ashes of each part, and likewise the amount of water, of organic and of inorganic matter in the juice. The results are given in the following table:—

	Leaves.	Rind.	Parenchyma.	Seeds.	Juice.
Potash	10·15	34·42	12·99	41·69	54·56
Soda	1·78	2·07	1·50	1 88	1 12
Lime	61·83	38·87	43·98	16·75	15 19
Magnesia	11·06	11·33	11·78	4·52	4·85
Sulphuric anhydride	4 85	3 44	3 69	3·39	1·94
Phosphoric anhydride	4·67	8·38	22 26	29·18	15·63
Silica	3·49	0·66	1·60	1·13	1·77
Undetermined matter and loss	2·17	0·83	2·20	1·26	1·64
	100	100	100	100	100
Ash in 100 parts of dry substance	12·36	6·982	2·130	2·821	

The leaves in the natural state contain 56·61 p. c. water, 38·03 organic, and 5·36 mineral substance; the juice contains 86·22 p.c. water, 12·32 organic, and 1·46 mineral substance. A lemon weighs on the average 75·3 grams, and contains in 100 pts.: 15·66 rind, 4·51 parenchyma, 1·06 seeds, and 78·77 juice.

The amount of potash in the ashes of the rind, seeds, and juice of the fruit is large, as is also the percentage of phosphoric anhydride in the ashes of the parenchyma and seeds. The author concludes his paper with a physical and chemical analysis of the soil in which the plants were grown.

C. E. G.

On the Leaves of Eucalyptus globulus. By A. Rabuteau (Compt. rend., lxxv, 1431).

An alcoholic extract of these leaves freed from resin by water acidulated with hydrochloric acid, and from tannin by a salt of iron, gives no precipitate either with iodine in potassium iodide or with phosphomolybdic acid. The author considers this a proof that the leaves contain no basic principle analogous to the alkaloids.

J. B.

Composition of Olive-Cake (Landw. Versuchs-Stationen, xv, 466).

A sample from Spain, which had been subjected, as usual, to two pressings for the extraction of the oil, had the following percentage composition:

Moisture	10·77
Albuminoids	8·56
Fatty matter	25·69
Crude fibre	28·64
Non-nitrogenous extractive matter	22·36
Ash	3·98

The cake is used in Spain as fuel. It may prove serviceable as a

cattle-food. More oil might probably be extracted with carbon sulphide.

R. W.

On the Function and Transformation of Fungi.

By A. Béchamp (Compt. rend., lxxv, 1199).

Under the term *fungi* the author includes all the organised forms, from molecular granulations to mycelium, which have appeared in the solutions examined: in this sense Bacteria and beer-yeast are fungi.

In one series of experiments upon an aqueous solution of cane-sugar, the following substances were used as ferments:—

1. Fungus developed in the filtered product of a normal alcoholic fermentation.
2. Microzymas, simple and coupled, produced in the washings of a sample of yeast.
3. Fungus, composed of microzymas, bacteria, and mycelium, formed in a water-butt.

In each case the products were alcohol and acetic acid, and the appearance of the ferment was unchanged. In a similar experiment with raisins covered with *oïdium*, alcohol and acetic acid were formed; and afterwards the ferment consisted of several forms of cells, many bacteria and other filiform ferments; but notwithstanding the presence of the latter, the amount of acetic acid formed was small.

Other experiments were made with the fungus which develops itself in solutions of pure tannin; with the microzymas which cause the liquefying of gelatin jellies; with the microzymas and small cells which are found in snuff, on the petals of *Robinia pseudo-acacia*, on the cornflower, &c. In each case alcohol and acetic acid are the normal products, and in some cases lactic acid appears, even without the presence of bacteria.

In a second series of experiments, fungi from various sources and moist yeast were added to creosoted solutions of cane-sugar; one only need be given. When a fungus was used which had been formed in a solution of tartaric acid, and consisted exclusively of a slender entangled mycelium, the tubes of which were filled with thin granulations, there was no disengagement of gas and no formation of alcohol, and only a very small quantity of acetic acid. The filaments of the mycelium were mostly disentangled, and there was no other product except free microzymas. The mycelium and microzymas from this experiment were then introduced into a mixture of the starch of fecula and moist yeast. In five days the starch was liquefied, and carbonic acid was disengaged. Three days afterwards all the mycelium filaments had disappeared, and in their place were myriads of microzymas, simple and coupled together, thus showing a retrogression of mycelium into microzymas analogous to that which takes place with beer yeast under the same conditions.

J. B.

On the Physiological Theory of Alcoholic Fermentation by Beer-yeast. By A. BÉCHAMP (Compt. rend., lxxv, 1036).

Two yeasts, apparently identical and pure, do not always yield the same results. Under the same conditions, yeast from the same lot always produces a like quantity of acetic acid; but, other things being equal, one sample of yeast may produce four times as much acid, or may require a period four or five times as long to complete the fermentation as another. Contact with the air, even with a large surface, far from augmenting the quantity of acetic acid, diminishes it, but generally shortens the period required for the fermentation.

In experiments made in apparatus where the air was displaced by a current of carbonic acid gas, from two to four times as much acetic acid was produced as in similar experiments made under exposure to the air. It is possible to produce in a saccharine solution a weight of acetic acid greater than the dry weight of the yeast used; the acid cannot therefore come from the yeast. The better the yeast is nourished in the solution, the less is the amount of acid produced. An increase of temperature shortens the duration of the fermentation, and augments the amount of acid. Pressure increases the quantity of acid.

J. B.

On the Power which Certain Substances possess of Preventing Putrefaction and the Development of Protoplasmic Life and of Fungi. By F. CRACE CALVERT (Compt. rend., lxxv, 1015; Proc. Roy. Soc., xx, 1872, 197).

IN experiments made upon a solution of albumin to which was added one-thousandth part of each of the substances whose antiseptic properties were to be studied, results were obtained which may be divided into four classes:—

1. Those substances which entirely prevent the development of protoplasmic life and of fungi: these are phenol and cresol.

2. Those which prevent the development of vibrios without stopping the production of fungi: zinc chloride, mercuric chloride, and zinc sulphophenate.

3. Those on the contrary which permit the production of vibrios, and prevent fungi: lime, quinine sulphate, pepper, and prussic acid.

4. Those which prevent neither the production of protoplasmic life nor of fungi: sulphurous, sulphuric, nitric, arsenious and acetic acids; caustic potash, soda and ammonia; solution of chlorine; sodium, calcium, and aluminium chlorides; calcium hypochlorite; potassium chlorate; calcium sulphate; ferrous sulphate; calcium bisulphate; sodium thiosulphate; sodium phosphate; calcium phosphate; potassium permanganate, potassium and sodium sulphophenates, picric acid; turpentine; wood-charcoal.

Acids, while not preventing the development of vibrios, facilitate the production of fungi: this applies especially to sulphuric and acetic acids. Alkalies, on the contrary, are not favourable to the production of fungi, but favour the development of vibrios. Zinc chloride and mercuric chloride completely prevent the development of animalcules,

but do not stop the formation of fungi. Chlorine and calcium hypochlorite only stop the production of vibrios when employed in great excess, and when calcium hypochlorite is so used, it acts with violence upon the proteic matters, producing a disengagement of nitrogen. Quinine sulphate completely stops the formation of fungi, and this fact leads to the supposition that, as quinine sulphate is remarkably efficacious in cases of intermittent fever, this malady may be caused by the introduction into the human economy of fungoïd bodies. This seems all the more probable when it is considered that this fever only exists in swampy countries where there is much decomposition of vegetable matter. Wood-charcoal possesses no antiseptic properties: it absorbs the putrid gases produced and causes their oxidation.

J. B.

Note on the origin of Bacteria, and on their relation to the process of Putrefaction. By H. C. Bastian (Proc. Roy. Soc., xxi, 129—131).

Analytical Chemistry.

Preparation of pure Sodium Silicofluoride, and its use in Volumetric Analysis. By F. Stolba (Zeitschr. anal. Chem., xi, 199).

A saturated solution of common salt, or rock-salt, is mixed with a quantity of silicofluoric acid sufficient to produce a copious precipitate. This precipitate, which consists mainly of sodium silicofluoride, but likewise contains, as silicofluoride, nearly all the potassium that was present in the common salt, is separated by filtration, and a portion of the filtrate is added to the silicofluoric acid to be used for precipitation. A precipitate of sodium silicofluoride is thereby formed which carries down with it all the silica dissolved in the silicofluoric acid. The liquid is then filtered; the pure silicofluoric acid thus obtained is mixed with the purified solution of sodium chloride; and the sodium silicofluoride thereby precipitated is washed by decantation with about ten times its volume of distilled water, till it no longer exhibits any chlorine reaction, and then thoroughly dried.

Pure sodium silicofluoride is recommended by the author for use in volumetric analysis. It reacts with alkalis in the manner shown by the equation—

$$2NaF.SiF^4 + 2Na^2O = 6NaF + SiO_2.$$

Consequently 47 grams of sodium silicofluoride will be decomposed by 1000 cub. cents. of a normal solution of caustic alkali. On account of the difficult solubility of the salt, however, it is best to use a decinormal solution (containing 4·7 grams in a litre).

H. W.

Mitscherlich's Test for Phosphorus. By O. Schifferdecker (Zeitsch. Anal. Chem., xi. 279—282).

The distillate obtained during the performance of Mitscherlich's test for phosphorus was oxidised by chlorine and precipitated by magnesia-mixture. This precipitate contained from 46·2 to 78·7 per cent. of the free phosphorus present in the original mixture.

It is, of course, necessary to continue the distillation till no more luminosity is observed in the condenser, and the luminosity should be confined to the condenser, as, if it takes place in the receiver, an undue loss of phosphorus is likely to take place.

T. B.

Volumetric estimation of small quantities of Arsenic and Antimony. By A. Houzeau (Compt. rend., lxxv, 1823).

It is well known that the trihydrides of arsenic and of antimony precipitate a solution of silver nitrate according to the equations—

$$12AgNO_3 + 2AsH_3 + 3H_2O = 12HNO_3 + 12Ag + As_2O_3,$$
$$3AgNO_3 + SbH_3 = 3HNO_3 + Ag_3 + Sb,$$

and the author proposes to utilise these reactions in order to estimate small quantities of these metals.

The gas generated in Marsh's apparatus is passed into a measured volume of silver solution of known strength, and when the precipitation is complete, the excess of silver nitrate is estimated by means of a standard solution of sodium chloride—

$$Ag = 0{\cdot}11574\ As. \quad Ag = 0{\cdot}1867\ Sb.$$

The arsenious acid may also be estimated directly by precipitating the excess of silver with hydrochloric acid, and titrating the filtered liquor with a standard solution of permanganate. Satisfactory test analyses are appended, showing that the method is capable of yielding trustworthy results.

J. W.

Colorimetric Method for the estimation of Manganese in Iron Ores, Cast-iron, and Steel. By P. Pichard (Compt. rend., lxxv, 1821—1823).

The method depends essentially upon the conversion of the manganese into an alkaline permanganate, and the subsequent comparison of the colour of the solution so obtained with that of a similar solution containing a known weight of manganese. The details are briefly as follow:—

0·1 gram of finely-divided material is first carefully oxidised by calcination, and then fused with 2 or 3 decigrams of sodium carbonate. The mass is dissolved in 5 c.c. of nitric acid, to which one drop of hydrochloric acid has been added, and the manganese is oxidised, after the addition of 10 c.c. of water, by boiling the solution for a short time

with 0·5 gram of lead peroxide. The clear liquor is subsequently decanted into a test-glass graduated into 500 c c. The standard solution of permanganate is prepared of such a strength that 10 milligrams of manganese are contained in 1 litre of the solution.

Specimens of iron, or of iron-ore, seldom contain more than 5 per cent. of manganese. If, therefore, 0 1 gram of material be taken for analysis, and the solution obtained therefrom be diluted until the tint corresponds exactly with that of the standard liquor, then every 100 c.c. observed will represent 1 per cent. of manganese in the sample under examination.

J. W.

Gravimetric estimation of Manganese. By R. FRESENIUS (Zeitschr. anal. Chem., xi, 290).

FINKENER objects to the estimation of manganese by precipitation of the solution (not too acid and free from ammoniacal salts) by sodium carbonate and boiling for a short time, on the ground that the precipitate always contains sodium salts; this Fresenius finds to be correct: these salts, however, can be thoroughly washed out from the ignited manganoso-manganic oxide by boiling water; moreover, after washing, manganese is always found in the washwaters, which must therefore be evaporated to dryness and treated with boiling water so as to regain the manganese contained in them Rose's method of precipitation as hydrate by caustic potash also causes manganese to be contained in the washwaters; the precipitate retains only traces of alkaline salts which can be readily washed out after ignition.

Precipitation as hydrated dioxide from acetic acid solutions by means of chlorine causes the formation of a little permanganate which must be reduced by means of alcohol; much alkaline salt is contained in the precipitate; this can *not* be perfectly washed out from the ignited precipitate by boiling water: hence the precipitate must be dissolved in hydrochloric acid, and thrown down again by ammonium sulphide or sodium carbonate.

C. R. A. W.

Analysis of Pig-iron and Steel. By F. KESSLER (Zeitschr. anal. Chem., xi, 249—270).

1. *Estimation of Iron.*—The author adopts a modification of the volumetric method depending on the use of potassium bichromate. Pure potassium bichromate is prepared by fusing the salt in a glass bulb placed in a bath of fused bichromate; the inner part of the salt thus prepared is found to be perfectly dry and undecomposed. A weighed quantity of this pure salt is added to the solution containing the iron (reduced to the ferrous state by the action of stannous chloride, excess of this latter being decomposed by the addition of mercuric chloride), and then a normal solution (4·91 gram per litre) of the bichromate is run in. The end of the reaction is noted by adding excess of bichromate, then a ferrous chloride solution till the blue colour with potassium ferricyanide reappears. If copper be present in any quantity, it must be removed by

precipitation with sulphuretted hydrogen, before the iron is estimated. The author, from his experiments, fixes the oxidation-equivalent of potassium bichromate as equal to 49·1.

2. *Estimation of Manganese.*—The following solutions are required:—

a. A decinormal potassium permanganate solution, containing 3·16 gram pure salt per litre.

b. An antimony chloride solution, prepared by dissolving 14·6 gram pure antimony oxide in concentrated hydrochloric acid, and diluting to 1 litre. This solution is titrated against the permanganate.

Solutions of sodium carbonate, sulphate, and acetate are required, containing respectively 200 and 500 grams of the crystallised salts per litre; concentrated and dilute acetic and hydrochloric acids, sulphur dioxide solution, and saturated bromine water must also be prepared.

·66 grm. of the iron or steel is dissolved, the solution diluted to 100 c.c., and neutralised with sodium carbonate solution, until a slight permanent precipitate is produced; this is dissolved by cautious addition of dilute hydrochloric acid: 1·2 c.c. concentrated sodium acetate solution and 1·2 c c. acetic acid, or in their place 3 c.c. sodium sulphate solution are then added, and the liquid, after dilution and boiling, is made up to 300 c.c. and filtered. 250 c.c. (= ·55 gram of the substance) are placed in a 600 c.c. flask; 150 c.c. water, 100 c.c. bromine water, and 2 c c. sodium acetate solution added; after an hour, 6 c c. of the latter solution are further added, and at the end of another hour, 12 c.c. of the same substance; the liquid is then warmed in the water-bath till all excess of bromine is driven off. The precipitate is collected and washed well with dilute sodium acetate solution. The filter, with the precipitate, is then treated in a porcelain basin with 5, 10, or 15 c.c. of the antimony solution, 15 c.c. strong hydrochloric acid are added, after a while, and the whole is digested till no trace of an undecomposed precipitate remains. 100 c c. water then are added, and the solution titrated with the permanganate solution. If the process is thus carried out, the difference between the number of c.c. permanganate corresponding to the c c. of antimony solution used, and the number of c.c. of permanganate actually employed, multiplied by ·5, gives the percentage of manganese (1 c.c. of the permanganate being equal to 0·5 per cent. manganese).

Cobalt, nickel, or copper, if present, are precipitated along with the manganese, but, except in the case of cobalt, their influence on the manganese estimation is scarcely perceptible.

M. M. P. M.

Estimation of the Ammonia contained in Coal-gas. By A. Houzeau (Compt. rend., lxxvi, 52—54).

The process recommended by the author consists in passing the gas through 5 c.c. of dilute sulphuric acid, containing ·30625 gram of H_2SO_4, until the liquid, which must be tinged with litmus, assumes a

blue colour. The current of gas is arrested, and the volume which has passed noted. It contains ·10625 gram of NH_3.

W. A. T.

Copper Solutions for the Estimation of Sugars.
By L. POSSOZ (Compt. rend., lxxv, 1836).

ON treating the different copper solutions employed in estimating sugars with acid carbonates of the alkalis, or with carbonic acid, some of the copper is precipitated, and a liquid remains containing alkali carbonate and alkali copper tartrate. This solution is not acted upon by pure cane sugar 60°—95° C.), while it is reduced by invert sugar. It also has no action whatever on cane sugar, and none, after reduction of its copper, upon excess of invert sugar present during the progress of the estimation. This, at least, appears to be what the author intends to assert, but his statements are somewhat ambiguous.

E. D.

Solubility Estimations in general, and Solubility of Cinchonine in Alcohol, Chloroform, and Mixtures of the Two.
By A. C. OUDEMANS (Zeitschr. anal. Chem., xi, 287).

THE author attributes the difference in the results obtained by various chemists in determining the solubility of substances to difference in the physical state of the body to be examined, to the existence of various isomeric or allotropic forms, and to the difficulty of keeping the temperature stationary for some time, so as to avoid supersaturation or imperfect saturation; also to impurity in the body and the solvent. In the case of cinchonine, he finds that alcohol and chloroform in a pure state can dissolve separately much less of the base than a mixture of the two can take up; at 17°, a mixture of 4 parts alcohol and 1 of chloroform takes up a maximum quantity, which is seven times as large as that taken up by absolute alcohol, and twenty times as much as that dissolved by pure chloroform.

C. R. A. W.

Testing of Quinine. By G. BIEL (Chem. Centralblatt., 1872, 630).

THE author was induced by the examination of an adulterated specimen of quinine sulphate, to investigate the methods of testing quinine. Liebig's method does not detect all the foreign alkaloïds of cinchona. Mann's test does not distinguish between cinchonine and cinchonidine. The author separates out the cinchonine from the salt dissolved in sulphuric acid, by means of ammonia and ether.

β-quinidine is detected by dissolving the specimen in Rochelle salt and adding ammonia; and cinchonidine in the residue dissolved in Glauber's salt.

Volumetrically the alkaloïds can be easily detected by Kerner's method, based on the different solubilities of the several freshly precipitated alkaloïds in ammonia.

G. T. A.

Estimation of Caffeine in Tea-leaves.

By E. LIEVENTHAL (Chem. Centralblatt., 1872, 631).

THE finely-powdered tea-leaves are heated for a few minutes with three times their quantity of chloroform, and when cold, the liquid is filtered off. The chloroform is then removed by distillation, and the residue is well washed with hot water and filtered; the filtrate, on evaporation, leaves a crystalline mass of caffeine. The author extracted sufficient caffeine from 20 grams of tea to give the characteristic reaction with chlorine-water and ammonia. He has proved the method to be capable of yielding quantitative results.

G. T. A.

New Method for the Determination of Urea.

By YVON (Bull. Soc. Chim. [2], xix, 3—6).

THE quantity of urea in urine can be very quickly determined by decomposing it with sodium hypobromite, and measuring the nitrogen thus set free.* The "uromètre" consists of a glass tube, 40 centim. long, the upper part of which (about one-fourth), is divided into tenths of c.c., and provided below this division with a glass stopcock. This tube dips into a wider one, serving as pneumatic trough. The apparatus being filled with mercury, a solution of 1 centig. of urea in 5 c.c. of water is introduced through the stopcock, and a little dilute soda is added, with which the pipette has been rinsed out. The solution of the hypobromite is prepared by dissolving 5 grams of bromine in 30 gr. of soda-lye and 12·5 gr. of distilled water. 5—6 c.c. of this solution are then put in; the reaction begins at once, and is finished by shaking the tube. After the vol. of nitrogen has been read off, the apparatus is again filled with mercury and 1 c.c. of urine, diluted with 4 c.c. of water, now treated in the same way. The quantity of urea found is always a little too high, because creatinine† and uric acid are also decomposed by the hypobromite; this is of little importance for clinical researches, a correction, however, may be applied by subtracting 4·5 from each 100 of the urea found. If an exact determination is required, the creatinine is removed by zinc chloride, the uric acid by basic lead acetate, and an excess of the latter by sodium phosphate. Creatinine and uric acid may also be determined by the same process, by making first a determination with the pure urine, a second after the creatinine has been removed, and a third after the precipitation of the uric acid. If the urine contains albumin, it has to be heated first in order to coagulate it.

C. S.

Determination of Free Acid in Fatty Oils. By M. BURSTYN (Zeitchr. anal. Chem., xi, 283).

100 c.c. of the oil to be examined are agitated with one or two volumes of 90 per cent. alcohol, and the whole is left at rest until the liquids

* A very similar method has already been proposed by Huefner (*Journ. Chem. Soc.* [2], ix.—C. S.

† In the original it is always printed creatine, which does not occur in urine, or in a very small quantity only.—C. S.

have separated. An aliquot part of the alcoholic liquor is then drawn off and titrated with soda-solution. Satisfactory results were obtained by thus analysing mixtures of olive oil and oleic acid.

T. B.

Chloroform as a Solvent and Means of Separation, for Vegetable Poisons in Forensic Investigations. By J. NOWAK (Dingl. polyt. J., ccvi, 422).

By shaking the solution, first made alkaline, with chloroform in the cold, the following are quickly and completely extracted: strychnine, quinine, quinidine, cinchonine, caffeine, theobromine, emetine, atropine, hyoscyamine, aconitine, veratrine, physostigmine, narcotine, codeine, thebaine, nicotine, and conine. More slowly are brucine, colchicine, and papaverine taken up from alkaline solution; with the aid of heat sabadilline, and in small quantity narceine. Picrotoxine goes over to the chloroform far more easily from acid than from alkaline solutions. Neither morphine nor solanine is taken up by chloroform. By shaking the alkaline chloroform solutions of the above bodies with dilute acids, the bodies themselves are obtained pure, leaving behind any fatty or foreign matters in the chloroform. A systematic process of separation is devised, based on these facts.

W. S.

Drying Chamber with Mica Walls. By A. C. OUDEMANS (Zeitschr. anal. Chem., xi, 289).

A HOT-AIR drying chamber with walls composed of mica plates $\frac{1}{4}$ to $\frac{1}{2}$ mm. thick, affords the means of observing how the drying progresses without chilling the inside by opening the door to inspect the substances inside the chamber.

C. R. A. W.

Apparatus for the Determination of Gases in Liquids. By E. REICHARDT (Zeitschr. anal. Chem., xi, 271—275).

THIS apparatus consists of a flask which is filled with the water to be examined, and is connected with a small gas-holder consisting of two bottles. This gas-holder being filled with air-free water, the sample in the flask is made to boil until the whole of the dissolved gases have passed over into the gas-holder, the water in the latter being by this time heated to the boiling temperature by the steam from the flask. Finally the gases are forced out of the gas-holder into a tube standing over mercury and treated in the usual way.

Successive examinations of the same sample gave concordant results.

T. B.

Technical Chemistry.

On Certain Injuries received by Thermometers during Transport. (Dingl. polyt. J., ccvi, 240—241).

In the carriage of parcels of thermometers, the boxes containing them are frequently overturned and shaken by accident, whereby a portion of the mercury in the instruments is separated from the main column and hangs in the upper part of the tube. It is generally easy to unite this portion of the mercury with that in the bulb by holding the thermometer vertically 2 or 3 inches above a piece of card, and letting it fall vertically upon the card, or whilst firmly holding it in the right hand, striking with the arm smartly against the palm of the left hand; or further the thermometer may be fastened to a piece of string and swung around, as with a sling, but with caution, and not too rapidly. In many cases the adhering particle of mercury is so small that its weight is not sufficient to overcome the adhesion to the side of the glass tube; the following plan of procedure is then recommended:—

The instrument is inclined at an angle of from 20 to 40 degrees, so that the bulb stands higher than the tube, and a blow with a flat piece of wood is given in the direction of the thermometer-stem. The mercury in the bulb is thus jerked forwards, and uniting with the detached portion fills the entire tube. If the thermometer be now slowly and cautiously brought into such a position that the mercury begins to flow back towards the bulb, the united column may generally be returned to its proper place. In the place where the separation has occurred, a small air bubble is generally found, as thermometers are seldom completely free from air, but by following the above recommendation, this difficulty may be almost always overcome.

W. S.

Salt Manufacture. By A. Patera (Chem. Centr., 1872, 632).

A paper contributed by the author to *Œsterr. Zeitung.*, v., 20, 289, on the possibility of producing a purer salt, with a smaller amount of bye-products, and of obtaining the latter in such a manner as to diminish the labour of fitting them for commercial purposes. This he thinks can be done at a less cost than at present, and without making any great change in existing arrangements.

G. T. A.

Contributions to the Theory and Practice of Sulphuric Acid Manufacture. By Fr. Bode (Chem. Centr., 1872, 632).

Headings of a paper by the author in Berg.-u. Hüttenm.-Z. 31, 315 on the production of heat in the combustion of different sulphides. Comparative value of different furnaces for roasting minerals containing sulphur, &c.

G. T. A.

Manufacture of Alkali. By J. J. Knight (Dingl. polyt. J., ccvi, 332).

Bone-ash or natural earthy phosphates are treated with sulphuric acid, soluble phosphate being obtained. Sufficient original material, in the state of fine powder, is now added to form the* bibasic calcium-phosphate, which is heated to bright redness with common salt or potassium chloride for several hours. By this process free hydrochloric acid and a nearly insoluble tribasic phosphate containing lime and soda or potash are produced. This insoluble phosphate boiled with a solution of the soluble calcium phosphate furnishes sodium or potassium phosphate, or with caustic lime yields solution of caustic alkali. The resulting tri-calcic phosphate is reconverted into soluble phosphate by means of sulphuric acid.

In another operation the quantity of mono- and tri-calcic phosphates is dried at 280°, whereby pyrophosphate is obtained, which is then heated to redness with salt, air or oxygen being passed over the mass. Free chlorine is thus obtained, and the insoluble phosphate above mentioned, which is treated with sulphuric acid as above, to form soluble phosphate.

W. S.

A New Process in the Preparation of Caustic Soda. By W. Helbig (Dingl. polyt. J., ccvi, 375).

†The object of this process is to economise sodium nitrate, which is otherwise used alone, to oxidise the sulphides in the caustic red liquors evaporated down in the manufacture of solid caustic soda. This economy is effected by blowing air through the red-hot fused caustic soda, obtained after evaporating with addition of a small proportion of nitre, and heating strongly again till the point is attained and just passed, when frothing up with evolution of ammoniacal fumes takes place. This point being passed, and the liquid having subsided, the caustic pot is heated still more strongly to bring the mass to a red heat, when it becomes quite fluid. Air is now blown cautiously in by a pipe reaching to the bottom of the pot, and pierced with holes up the length, but closed at the extremity; the caustic is blown as vigorously as possible, care being taken that the ripples formed in the liquid do not rise too high. Samples of the caustic are taken from time to time and examined. When the oxidation is complete, a pure white product sometimes faintly tinged with blue, is obtained on cooling a sample.

W. S.

Preparation of Potash, Soda, or Baryta from the corresponding Sulphides. By Tessié du Mothay (Dingl. Polyt. J., ccvi, 333).

The sulphides are treated with lead oxide, and the lead sulphide formed is decomposed by hydrochloric acid, the liberated hydrogen sulphide

* This so-called "bibasic calcium-phosphate" has the formula $Ca''HPO_4$, and is therefore, it need hardly be stated, a tribasic phosphate, as is also the so-called monophosphate $Ca''H_4(PO_4)_2$.—W. S.

† A process almost identical with the one here described is used in most of the large alkali works in South Lancashire, where caustic soda is manufactured.—W. S.

being burnt and the sulphurous oxide economised, whilst the lead chloride is re-converted into lead oxide by means of lime or magnesia. If magnesia be used, hydrochloric acid is regenerated by heating the magnesium chloride to redness in a current of steam.

By another operation, the sulphides are decomposed by boiling with water and silicofluoride of sodium or barium. Hydrogen sulphide is liberated and silica precipitated, whilst the alkalis remain in solution as fluorides. The latter are decomposed by lime or calcium carbonate, or, the fluorides are treated with barium carbonate, and carbonic acid is passed through, and thus barium fluoride and alkaline carbonate are obtained. The former is converted into barium hydrate by means of lime.

In a more recent addition to his patent, the author substitutes zinc oxide for lead oxide, since zinc sulphide is more easily decomposed by hydrochloric acid, and by roasting or treatment with nitric acid zinc sulphate is readily obtained. By boiling with sodium chloride solution sodium sulphate and zinc chloride are formed, and the zinc chloride may be converted into zinc oxide by means of lime or magnesia.

W. S.

Recovery of Potash, Soda, &c., from Soap-water. By Tessié du Motiay (Dingl. polyt. J., ccvi, 333).

The soap-water is decomposed by calcium, barium, or magnesium carbonate, and carbonic acid passed through the liquid. The bicarbonate formed precipitates organic matter and other impurities, and these settle down. The solution is then evaporated, or treated with baryta-water, which precipitates the last portion of foreign matters, and leaves a solution of caustic alkali.

At a particular stage of the process, the author uses an acid in order to hasten the separation of the resinous substances, and in certain cases of the sulphides of sodium and calcium, or barium and calcium, or ferric oxide, and then passes carbonic acid into the liquid. The precipitated metallic sulphides carry down with them the humus-like substances present.

W. S.

Softening of Water by Boiling with Lime. By J. Stingl (Dingl. polyt. J., ccvi, 304—312).

The author refers to his former paper (see this Journal, 1872, 272). He points out that an excess of lime must be avoided. To determine the amount of lime necessary to be added, he titrates lime-water against a decinormal nitric acid solution coloured with litmus until neutral. The amount of lime (CaO) in 1 cub. centimeter of the solution is thus ascertained.

This standard lime-water is then run, from a burette, into 100 cubic centimeters of the water under examination until a *flocculent* precipitate begins to form; at this point the water should show an alkaline reaction with turmeric paper (by Pettenkofer's method). From the

number of cubic centimeters used the amount of lime is calculated, and this may be reduced to dry lime per cubic foot of water.

M. M. P. M.

Ransome's New Artificial Stone. (Dingl. Polyt. J., ccvi, 332.)

THE following mixtures give three qualities of a very hard and durable cement, capable of resisting the action of the weather. It is very suitable for cementing fractures in marble or stone images, monuments, or ornamental work, which are exposed in the open air.

	No. 1.	No. 2.	No. 3.
Portland cement	12 parts.	6 parts.	9 parts.
Chalk paste	6 "	12 "	6 "
Fine sand	6 "	6 "	6 "
Silicious earth	1 "	1 "	1 "

The above mixtures were made into a thick paste with soda water-glass. No. 2 gave the hardest cement, and No. 3 the coarsest grain.

W. S.

Kieserite, its Properties and Applications. By H. GRÜNEBERG (Deut. Chem. Ges. Ber., v, 840—842).

KIESERITE ($MgSO_4.H_2O$) occurs as an essential constituent of the Abraumsalz of Stassfurth, which contains about 12 per cent. of it. It is difficultly soluble in cold water, and on this depends the possibility of separating it from the Abraumsalz.

After boiling down the solution of the Abraumsalz to extract the potassium salt, the residue is placed in a funnel-like vessel and washed with cold water; this separates the soluble salts from the mixture of other partially soluble compounds, kieserite, anhydrite, clay, sludge, &c., which may be separated to a great extent by their difference of specific gravity. The kieserite is then placed in iron frames and crystallised by heat. In this process a part of the compound is converted into the salt containing 7 mol. of water, and the mass is sent into commerce as block kieserite containing 60 per cent. $MgSO_4$. One of the principal uses of this kieserite seems to be for the washing of wool; it is also used for the preparation of "permanent white" by precipitation with barium chloride, and for the manufacture of crystallised glauber salts with the rock salt, which is a bye-product of the Abraumsalz. 2 molecules of kieserite and 1 of calcium hydrate heated with water, solidify to a gelatinous mass containing $CaSO_4 + MgSO_4 + MgO$. This on being strongly heated, powdered, and mixed with water, quickly hardens to a marble-like mass which has many valuable properties; it polishes and withstands the damp to a certain degree.

A. P.

Methods of Extracting Silver in Mexico. By LAUR (Chem. Centr., 1872, 650).

THE author describes the cost of the various methods in use for extracting silver from different ores, and the loss involved in each case,

and concludes that if a simple process applicable to all classes of ore could be invented, the production of silver in Mexico would be much greater than at present.

G. T. A.

Monnier's Process for Copper Extraction. (Dingl. polyt. J., ccvi, 331.)

The sulphuretted copper ores are roasted with soda, whereby, besides acid sodium sulphate, ferrous and cupric sulphates are formed. By stronger heating, the excess of acid in the sodium salt acts upon the metallic sulphides, and then follows decomposition of the ferrous sulphate. The copper salt, whose solubility is favoured by the presence of the sodium salt, is washed out and the solution is evaporated to the crystallising point. About four-fifths of the sodium sulphate then crystallise out, and the mother-liquors are further evaporated, when cupric sulphate crystallises with a little sodium sulphate. The cupric sulphate thus obtained is now dried and heated in a furnace with coal to a red heat, after which the sodium salt is washed out from the remaining cupric oxide and metallic copper. In this process the iron for precipitating the copper is saved, and not more than 1 per cent. of sodium salt is lost. From a pyrites containing 85 pounds per ton of copper, 82½ pounds of metal were actually obtained by this process.

W. S.

Amount of Arsenic in Pyrites and its Distribution in Acid and Alkali-manufacture. By H. A. Smith (Phil. Mag. [4], xliv, 370—381).

The author believes the amount of arsenic in pyrites to be greater than is usually supposed. He has analysed several different kinds, and has traced the distribution of the arsenic during the manufacture of acid and alkali therefrom. Accordant analyses gave the following mean percentages, reckoning the arsenic, in every case, as arsenious oxide:—Spanish pyrites (*a*) Tharsis's, 1·65; (*b*) Mason's, 1·74; Belgian, 0·94; Westphalian, 1·88; Norwegian (*a*) Hard, 1·65; (*b*) Soft, 1·71; deposit in the flue leading from the pyrites-kilns to the lead-chamber, 46·36; deposit in the chamber, 1·86; sulphuric acid, 1·05; hydrochloric acid, 0·69; sodium sulphate, 0·03; soda-waste, 0·44; sodium carbonate, none; recovered sulphur (*a*) Mond's process, 0·70; (*b*) After purification, none. For the further distribution of the arsenic, see this Journal [2], x, 1132.

Several unsuccessful attempts were made to free sulphuric acid from arsenic on the large scale. Hydrosulphuric acid was found to be too expensive, besides being a "nuisance." Ferrous sulphide, though an excellent purifier of acid employed in wire-working and galvanising, is not adapted for acid used in bleaching, dyeing, or printing. Sodium sulphide acted very well and at a moderate expense, but the excess of gas could not be easily disposed of. Sodium chloride and hydrochloric acid act only partially, the latter being also very expensive. Acid is often condemned as unfit for use owing to the supposed presence of

iron, while the mischief is frequently caused by arsenic. Makers of ammonium sulphate have suffered great losses from this mistake.

B. J. G.

New Process for the Manufacture of Steel. By BAJAULT and ROCHE (Compt. rend., lxxvi, 80).

A MIXTURE of powdered ore and molten cast-iron is cast in moulds made of metal; the ingots thus made, of which the moulds form part, are then heated in a peculiar furnace to a bright-red heat for some time; carbon oxide is evolved and ingots of crude steel are formed; these only require melting in crucibles or a reverberatory furnace to be fit for use. The action of the ore upon the walls of the furnace is thus avoided, and thus the principal objection to the use of rich ores is got rid of.

All degrees of carburation may be obtained by this process, the proportions of cast-iron and oxide being determinable with almost mathematical precision. A sample thus prepared by it, half-hard, malleable and tenacious, and acquiring great hardness by tempering, was found to have the following composition:—

Carbon			
combined.	uncombined.	Silicon.	Sulphur and Phosphorus.
0·430	0·080	0·230	none.

C. R. A. W.

To Produce Diamond Hardness in Graving-tool Steel and Steel Wire. By J. SCHÜSZLEDER (Dingl. Polyt. J., ccvi, 419).

WATCH and clock makers and engravers harden their steel in sealing-wax. The article is made white-hot and thrust into sealing-wax, allowed to remain a second, then withdrawn, and again inserted in another part, and this treatment is continued till the steel is cold and will no more enter the wax. The hardness thus attained is extreme, and comparable to that of the diamond; in fact steel hardened by other processes may be engraved or bored with it, the engraving or boring tool being previously moistened with oil of turpentine.

W. S.

A Simplification of the Method of Gilding Iron by the Dry Process. By W. KIRCHMAN (Dingl. Polyt. J., ccvi, 419).

SODIUM-AMALGAM was found an advantageous means of simplifying the method of dry-gilding iron, and for painting gold designs thereon. By simply rubbing with this amalgam, the surfaces of iron and similar metals, although oxidised, are immediately amalgamated. Gold chloride in concentrated solution is then applied quickly on the amalgamated surface, and the mercury volatilised by the heat of lamp or fire. A very uniform gilding is thus obtained admitting of high polish. With silver- and platinum-salts corresponding results are obtained.

W. S.

Silvering of Glass. By R. SIEMENS (Dingl. Polyt. J., ccvi, 419).

As a reducing agent, acetic aldehyde is used in the form of aldehyde-ammonia, prepared by passing dry ammoniacal gas into aldehyde. Four grams of silver nitrate and $2\frac{1}{2}$ grams of aldehyde-ammonia are separately dissolved in a litre of distilled water and the solutions mixed and filtered. The article to be silvered, after washing out with solution of potassium carbonate and then with spirits of wine and distilled water, to remove every trace of grease, is filled with this solution (as far as it is desired to silver) and then hung up in the water-bath. It is now gradually heated, and as soon as the temperature reaches 50°, the separation of the silver mirror begins, and soon spreads over the whole inner glass surface. Its formation is soon finished, usually between 55° and 60°. When the beauty of the silvered surface reaches a maximum, it is time to withdraw the article from the water-bath and pour off the contents, or the brilliancy of the mirror will be impaired. The article is finally rinsed in distilled water.

W. S.

On Coal-tar and Pitch. By E. A. BEHRENS (J. pr. Chem. [2], vi, 277—300).

THE composition of coal-tar varies considerably with the temperature at which coal is distilled; *the higher the temperature, the larger is the yield of solid bodies.* Tar produced in gas-retorts contains more benzene and toluene, but also more naphthalene and other solid hydrocarbons than that obtained by distilling coal in Pauwel's coke-furnaces; the latter tar contains chiefly liquid hydrocarbons and a *considerable quantity of compounds* soluble *in alkalis, but only a very small quantity of carbolic acid.* When heavy coal-tar oil is allowed to run into a furnace heated to a bright-red heat, it yields, besides naphthalene, 2 per cent. of benzene and toluene and a little xylene, but only traces of higher homologues. At a lower temperature the decomposition of the oil is less complete, and at a higher, the benzene is converted into naphthalene. In the furnace there remains a kind of graphite, which is a very valuable fuel for producing high temperatures.

The pitch which is left behind in the distillation of tar is partially soluble in benzene and carbon sulphide; the residue consists of a black powder, having the composition of Welsh anthracite. When pitch is passed through a red-hot tube it yields about 250 vol. of a gas consisting almost entirely of hydrogen; but on distilling it from a retort it yields about 25—30 per cent. of an oil containing pyrene, chrysene, and anthracene. The other products consist of 0·2 per cent. of light oils and gases containing ammonia and hydrogen, and 48—52 per cent. of coke is left behind. In some works the pitch is distilled with over-heated steam in order to obtain anthracene; in this case the residue is a very brittle pitch, which is mixed with naphthalene, and then used like the undistilled pitch, as asphalt or as fuel, by mixing it with coal-dust and forming the mass into bricks, and for other purposes.

C. S.

Artificial Fuel from Coal-dust. By E. F. LOISEAU (Chem. Centr., 1872, 559).

DUST of bituminous coal or anthracite is mixed with about 7 per cent. of plastic clay and made up into bricks, which are dipped into ordinary benzol containing colophony in solution They are then exposed to a current of air, whereby the benzol is evaporated and a coating of rosin is left on the surface which renders the coal-bricks perfectly water-tight.

H. W.

Explosions in Flour-mills. (Dingl. Polyt. J., ccvi, 417.)

OF the various explanations which have been offered to account for these explosions, there are two worthy of attention, viz.:—

1stly. The rapid combustion of the finely divided flour; and,

2ndly. The ignition of a mixture of air with gases furnished in the decomposition of the flour.

It has been found that flour and bran intimately mixed at 450°, give off a gas which, mixed with 9 volumes of air, forms an explosive mixture that may be ignited by a spark. Wiebe is of opinion that when the apparatus of the exhauster in a flour-mill becomes very dry, such a temperature may be attained as to favour the production of this gas. The stones, which in grinding bran are very close together, strike sparks, which, carried by the current of air behind the exhauster, ignite the gas. In the combustion of wood, flour, &c., carbon dioxide and steam are formed, which at that high temperature occupy a much greater space than their elements before the combustion. Now, if a flame approach too near a mixture of air and fine wood-dust, so that some of the minute particles of dust take fire, the heat set free enables some of the neighbouring particles also to ignite, and the combustion passes almost instantaneously through the entire space and seizes upon the boards, beams, &c., of the place, and the gaseous products of the combustion of the dust, by their rapid formation and expansion, produce an explosion. An explosion arising precisely in this manner occurred in a room in the Town-hall of Friedck, by which five persons were seriously injured.

That when flour is mixed with air, and a candle is brought in contact with the mixture, it will ignite and fire off, has lately been often observed. An explosion thus occurred in the Ofen-Pesth Steam-mill, destroying windows and roof. During the mixing of some very fine varieties of flour, the door of the mixing-room had been left open by a workman, and the thick cloud of flour-dust, as it spread around, ignited at a flame.

If the stones are placed too close they strike occasionally, producing sparks, and these ignite a small portion of the cloud of fine particles of flour and bran surrounding the apparatus, the motion of the elevator promoting the combustion by creating a current of air. The combustion thus favoured passes instantly through the whole room, and the explosion follows. The use of exposed portable lights in flour-mills ought to be strictly prohibited. A violent explosion occurred last

year in a mill through the contact of the flame of an oil-lamp without cylinder, with a circulating cloud of flour-dust.

The great Glasgow explosion of last year is attributed to an accidental cessation of the feeding of the stones, the latter striking sparks which, kindling the flour-dust in the exhauster, resulted in the blowing up of the exhauster case, the flame spreading throughout the whole mill.

Spontaneous combustion, in presence even of considerable warmth, has certainly never been observed in storehouses containing large masses of flour.

W. S.

Arsenic in the Air of Rooms. By Prof. FLECK (Zeitschrift. f. Biologie, viii, 444—456).

IN spite of all legal enactments to the contrary, pigments containing arsenic continue to be used for carpets, wall-paper, and coloured washes, more especially the compound of copper and arsenic known as Schweinfurt green. Hence arise frequent cases of arsenic poisoning. It has been stated that in rooms in which Schweinfurt green has been used as a pigment, a fine dust containing arsenic and copper is produced, which, acting on the capillaries of the lungs, produces the symptoms of poisoning. But it is also said that a gas containing arsenic is developed from arsenic pigments, and that there is evidence of this in the garlic-like smell of the air in the rooms where these pigments are used. The author has endeavoured, by numerous experiments, to show why and under what conditions such a gas can be developed. Schweinfurt green, taken as the type of arsenic colours, contains, in addition to arsenite and acetate of copper, more or less free arsenious acid, according to the more or less careful manner of its preparation. Organic matter and moisture act upon this free acid so as to produce arsenetted hydrogen, and this is more especially the case when such substances as starch-paste and gelatin are used with it as cements to fasten the paper on the walls, etc.

A similar phenomenon may take place in aniline dyes containing arsenic.

G. T. A.

Economy of Indigo in Printing Blues. (Dingl. polyt. J., ccvi, 334.)

With Yellow, Green, and Orange.—Next to the indigo vat is placed a vat containing a decoction of catechu in water. The fabric to be coloured is printed with the yellow or green paste; for green it must have previously received a blue tint. It is next placed in the catechu vat, where it is allowed to remain some time, but not so long that the printed paste begins to be dissolved. The fabric is now placed in the indigo vat, and dyed to the desired extent. The final treatment with potassium chromate solution brings forward the catechu tint, and produces, with the indigo blue, a dark indigo ground.

For Light Blue and White.—Two vats are used, one containing a

decoction of 12 pounds of logwood extract with 600 litres of water, the other, a solution of 6 pounds of cupric sulphate in 300 litres of water. The fabric printed with the protecting paste is stretched on the frame and allowed to sink in the logwood vat; after which it is placed in the copper vat, and then returned to the logwood bath; 6 pounds of alum are now added to the copper bath, and the piece is once more placed therein. Care must always be taken that the protecting paste is not disturbed. The piece is finally stretched, and cleansed in a bath containing a solution of 12 pounds alum in 300 litres water. If an indigo tint be required, the printed and stretched piece is first placed in the indigo vat and then in the logwood and copper baths.

W. S.

Blue Dyeing. By GRÄFE (Chem. Centr., 1872, 743).

THE oxalates are known to prevent the precipitation of Prussian blue. By mixing the solution of an iron salt, therefore, with a neutral oxalate and potassium ferrocyanide, a clear bluish-green solution is obtained. Goods immersed in this solution, and then, without wringing, dipped into water acidified with hydrochloric acid and containing a little tin chloride, are dyed blue immediately.

W. A. T.

Anthracene Blue. By F. SPRINGMÜHL (Chem. Centr., 1872, 728).

THIS new colouring matter is a bye-product of the manufacture of alizarin; it has yet only been prepared in small quantity. The colour is soluble in water, and dyes silk, wool, and cotton of a splendid and permanent blue.

R. W.

Preparation of Fuchsine without Arsenic.
(Dingl. polyt. J., ccvi, 312.)

COMMERCIAL aniline treated with nitrobenzene yields rosaniline.

$$\underset{\text{Toluidine.}}{2\{C_6H_4(NH_2)CH_3\}} + C_6H_5(NO_2) = \underset{\text{Rosaniline.}}{C_6H_4(C_7H_6)_2N_3H_3} + 2H_2O.$$

M. M. P. M.

Iodine Green on Linen. (Dingl. polyt. J., ccvi, 334.)

EIGHT pounds of sumach are boiled in water, and the fabric is placed in the solution over night. It is then mordanted in a solution of aluminium acetate, made by adding a solution of 1 pound of alum to one of $1\frac{1}{2}$ pounds lead acetate. The material is now dyed in the iodine-green, which is obtained by dissolving this colouring matter in the form of powder, which must be of good quality. If requisite, the shade may be modified by subsequent treatment in a weak picric acid bath; 60 pounds of yarn require 1 pound of the iodine-green powder.

W. S.

Deep Red on Cotton with "Rouge de Tournai."
(Dingl. polyt. J., ccvi, 334.)

THIS colouring matter is obtained as a paste. To dye cotton with it, the bleached cotton first receives a strong "Orleans" ground tint, is then washed, and placed in a bath of aluminium-acetate solution, in which it remains six hours, when it is afterwards dyed in a warm bath of "Rouge de Tournai." By using more or less of the dye, a lighter or deeper shade may be obtained.

W. S.

A Blue Stamp Colour. By R. BOTTGER
(Chem. Centr., 1872, 743).

BLEU de Lyons is dissolved to saturation with the aid of gentle heat in concentrated glycerin, some Thénand's blue added, and the liquid thickened with finely powdered gum arabic.

W. A. T.

A New Process for Colouring Ivory, Gelatin, Feathers, etc., a fine Red. By C. PUSCHER (Chem. Centr., 1872, 743).

WHEN picric acid is mixed with a solution of magenta, decomposition takes place. But by adding to each, before mixing, a quantity of ammonia, a deep yellow solution is obtained which colours wood, leather, silk, etc., a brilliant red.

W. A. T.

Wood Staining (Chem. Centr., 1872, 526).

(1.) *Ordinary Black Staining.*—Brazil wood, powdered gall-nuts and alum are boiled in water until a black colour is obtained; the liquid is filtered and spread upon the wood which is then covered with a preparation of iron filings heated for some days with vitriol and vinegar. It then becomes of a fine black colour.

(2.) *Staining Fine Woods.*—Applicable especially to apple, pear, and walnut woods. 4 oz. gall-nuts, 1 oz. powdered logwood, $\frac{1}{2}$ oz. vitriol, and $\frac{1}{2}$ oz. verdigris are boiled with water, and the solution, filtered hot, is applied to the wood, which is then coated with a solution of 1 oz. fine iron filings dissolved in wine vinegar.

Inlaid wood is treated with a liquid prepared by mixing $\frac{1}{2}$ oz. sal-ammoniac with a quantity of steel filings, adding vinegar, and leaving the mixture for fourteen days in a warm oven. In this liquid the wood is boiled, and then allowed to remain therein for three days; it is then similarly treated with a mixture of gall-nuts and Brazil wood decoction.

M. M. P. M.

Process for the Preservation of Albumin for Photographic Purposes. By W. ZAY (Chem. Centr., 1872, 743).

WHITE of egg is beaten to a stiff froth, and then set aside. After some time the albumin dries hard. For use it has simply to be rubbed up with a little water and the solution strained.

W. A. T.

Carbon-pictures on Gypsum or Earthenware Plates.

By Rich. Jacobsen (Chem. Centralblatt., 1872, 634).

Prepared paper is exposed for a sufficient time under a transparent drawing, woodcut, etc., and the excess of chrome-salt removed by washing. The paper is then transferred, picture-side down, to a plate of gypsum. A positive copy is thus obtained from a positive drawing, as only the unaltered gelatin sinks into the gypsum. By replacing the carbon with enamel-colours, designs can be printed on and burned into unglazed porcelain, etc.

G. T. A.

Photography:—*H. Vogel on Dry-plate Photography and Sensibilisers.* (Chem. Centr., 1872, 795.)—*E. Baudrimont: Nature of the White Spots which often appear on Photographs.* (J. Pharm. Chim. [4], xvi, 341; Chem. Centr., 1872, 795.)—*Hemberg: Preparation of Carbolic Acid Paper.* (J. Pharm. Chim. [4], xvi, 363; Chem. Centr., 1872, 796.)—*Chardon: Dry Plates with Uranium Bromide.* (Phot. Arch., xiii, 141; Chem. Centr., 1872, 618.)—*E. Anderson: Rectification of the Negative Silver-bath.* (Phot. Arch. xiii, 216, 229; Chem. Centr., 1872, 823.)—*J. Towler: The Albertotype.* (Chem. Centr., 1872, 810.)

Preparation of Active Bone Black. By Dr. Graeger (Dingl. polyt. J., ccvi, 472—474). Mere directions to exhaust ordinary animal charcoal with hydrochloric acid, and to wash well.

C. H. G.

Process for rendering Tallow fit for Food. By J. Casthelaz (Dingl. polyt. J., ccvi, 474). The free fatty acids are removed by boiling with a solution of sodium carbonate, and the soaps so produced washed out with water.

C. H. G.

Process for Purifying and Decolorising Beet-root Juice. By Tessiè du Mothay (Dingl. polyt. J., ccvi, 499). The juice, syrup, &c., is heated with lime (1—2 per cent.), and one-half or two-thirds of this reagent again precipitated by the addition of bisulphite of magnesia or lime. The remainder of the lime is then thrown down (? after filtration) by further addition of the same sulphites or of sulphite of alumina.

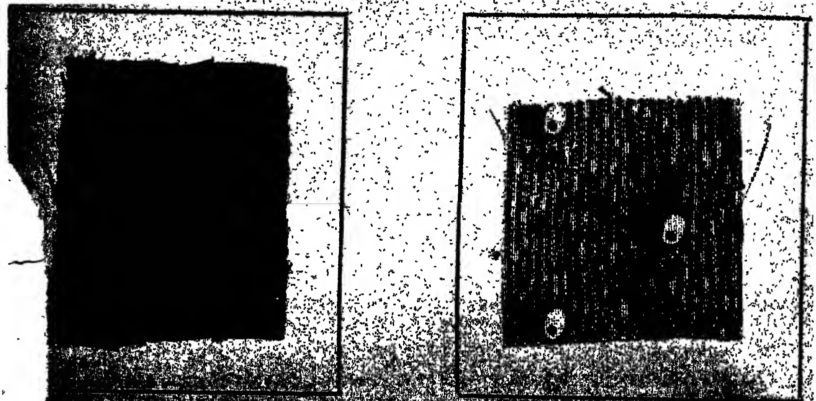
C. H. G.

"Schrotbrod," its Composition and Preparation, and its relation to Health. By H. Vogel (Dingl. polyt. J., ccvi, 480—485). Whole meal bread made without yeast or leaven, like oat cake.

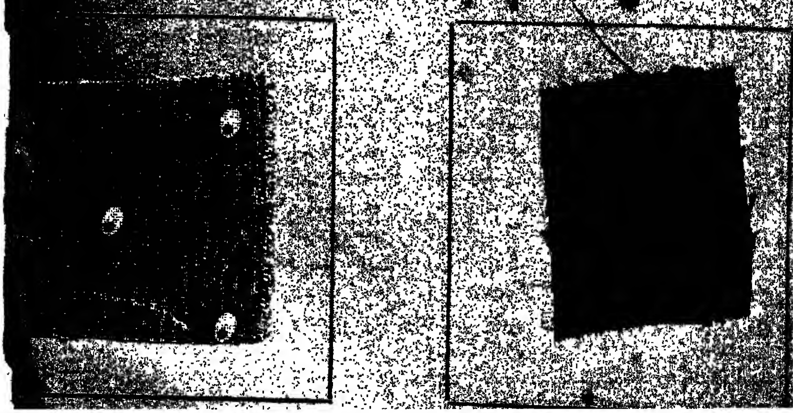
C. H. G.

On Poisoning of Bread (Dingl. polyt. J., ccvi, 475—480).

DYED WITH ALIZARIN.



DYED WITH ANTHRAPURPURIN.



PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XV.—*On Anthrapurpurin.*

By W. H. PERKIN, F.R.S.

COMMERCIAL artificial alizarin, when introduced as a dyeing agent, was generally supposed to contain purpurin, owing to the pureness of the red colours it produced with alumina mordants (vol. xxiii, p. 143), but in a paper which I had the honour of reading before the Society some time since, this idea was shown to be incorrect; in the same paper, however, the existence in this product of a colouring matter differing from alizarin was pointed out. I have been for some time experimenting with this substance, and in August last brought a short account of it before the Society (vol. xxv, p. 659). I now beg leave to give a more detailed account of the results I have obtained in its examination.

To obtain this substance, which I propose to call *anthrapurpurin*, from commercial artificial alizarin, I have tried various methods, amongst these repeated crystallisation from solvents; but this has not enabled me to separate it perfectly from the alizarin and other products with which it is associated, although its solubility differs considerably from them. I was, therefore, obliged to have recourse to chemical processes for its separation.

In the paper already referred to, I mentioned that this substance differed from alizarin in the behaviour of its alumina lake when treated with an alkaline carbonate, the colouring matter being in this case dissolved out by the alkaline solution, whilst the alizarin lake remained unattacked. I find that this process succeeds very well, except that the filtrations are extremely tedious. Instead, however, of converting the commercial alizarin into a lake as I previously did, and then treating it with an alkaline carbonate, I find it more convenient to dissolve the crude colouring matter in dilute sodium carbonate, and then well agitate the resulting solution with freshly-precipitated alumina, which combines with the alizarin, leaving the anthrapurpurin in solution. This is filtered off from the alizarin lake, heated to boiling, and acidified with hydrochloric acid. The colouring matter which is precipitated is then collected on a filter, washed, and dried.

The anthrapurpurin thus obtained is very impure, being associated with a substance dyeing alumina mordant of an orange colour,* as well as anthraflavic acid, &c.

* This is under investigation

These impurities can be removed to a considerable extent by repeatedly boiling the product with alcohol, anthrapurpurin being but little soluble in that menstruum. I have usually performed this operation nine or ten times; but the residual product, after crystallization from glacial acetic acid, has not given very satisfactory results, although analysed several times. To further purify it, I have found it best to digest it with boiling alcoholic soda, and collect the difficultly soluble sodium-compound which forms on a filter and wash it several times with dilute alcoholic soda. This is then dissolved in water, boiled, and the colouring matter precipitated with barium chloride; the purple barium compound thus obtained is collected on a filter, washed a few times with hot water, and then decomposed by boiling with sodium carbonate; the resulting purple solution is filtered off; and the anthrapurpurin precipitated with hydrochloric acid. After this has been collected on a filter, it is well washed with water, dried, and finally twice crystallised from glacial acetic acid.

The specimens used in the subjoined analyses were not all prepared by the process just described; in some, the treatment with alcoholic caustic soda was dispensed with, and in others the colouring matter was precipitated with zinc acetate instead of barium chloride, &c.; but I regard the above process as the most certain I have used. The specimens analysed were mostly dried at temperatures above 100° C., and some as high as 180° C.—190° C

I. ·2240 of substance gave
·5424 of CO_2, and
·0700 of H_2O.

II. ·2025 of substance gave
·4894 of CO_2, and
·0594 of H_2O.

III. ·2560 of substance gave
·6130 of CO_2, and
·0760 of H_2O.

IV. ·3591 of substance gave
·8572 of CO_2, and
·1055 of H_2O.

V. ·2412 of substance gave
·7577 of CO_2, and
·0707 of H_2O.

VI. ·3237 of substance gave
·7800 of CO_2, and
·0935 of H_2O.

VII. ·3012 of substance gave
·7234 of CO_2, and
·0870 of H_2O.

VIII. ·3756 of substance gave
·9107 of CO_2, and
·1102 of H_2O.

IX. ·2518 of substance gave
·6070 of CO_2, and
·0723 of H_2O.

X. ·2363 of substance gave
·5678 of CO_2, and
·0681 of H_2O.

XI. ·3182 of substance gave
·7608 of CO_2, and
·0910 of H_2O.

XII. ·2645 of substance gave
·6335 of CO_2, and
·7580 of H_2O.

These numbers give percentages agreeing with the formula—

$$C_{11}H_8O_5,$$

as the following comparisons show :—

	Theory.		Experiment.			
			I.	II.	III.	IV.
C_{14}....	168	65·62	66·03	65·91	65·30	65·1
H_8....	8	3·12	3·47	3·26	3·29	3·26
O_5....	80	31·26	—	—	—	—
	256	100·00				

Experiment (*continued*).

V.	VI.	VII.	VIII.	IX.	X.	XI.	XII.
65·11	65·71	65·5	66·12	65·74	65·53	65·2	65·31
3·25	3·20	3·2	3·25	3·19	3·20	3·17	3·18

NOTE.—The substance employed in Analysis I was obtained by repeatedly crystallising crude anthrapurpurin, after digestion with alcohol. That employed for No. II was obtained from a similar product, but purified by conversion into a zinc compound; and that used for No. VIII was also obtained from crude anthrapurpurin by precipitating its alkaline solution with barium chloride, the product obtained from the precipitate being afterwards crystallised from carbolic acid.

Anthrapurpurin when heated, at first fuses and then evolves orange-coloured vapours, which condense as yellowish-red leaves or needles, but by far the largest quantity of the substance is carbonised. It is difficultly soluble in alcohol and ether, but rather more soluble in glacial acetic acid. It is deposited from the boiling acetic solution on standing in small fungoïd-looking groups of minute orange-coloured needles. These groups are generally not more than 2 or 3 m.m. in diameter, and from the direction of the crystals, generally appear lighter on the under side than on the upper. They can only be seen to advantage under the microscope. As this substance dissolves but slowly in boiling glacial acetic acid, it is sometimes necessary to distil off part of the acid before the resulting solution can be made to deposit crystals.

Anthrapurpurin is very slightly soluble in water, and may be removed from its aqueous solution by means of ether. When heated with powdered zinc, it yields a hydrocarbon in small quantities, which, when purified, has the fusing point and other properties of ordinary anthracene.

Anthrapurpurin and Acetic Anhydride.

From the foregoing analyses, and bearing in mind that anthrapurpurin is an anthracene derivative, very little doubt could be entertained as to the correctness of the formula assigned to it. Nevertheless, I thought it desirable to confirm it by the study of some of its compounds. Being unsuccessful in getting any satisfactory results from the examination of the products obtained by precipitating its solutions with metallic salts, I thought that possibly it might yield an acetylic derivative of a definite character; in this I was not disappointed. Anthrapurpurin heated under pressure with acetic anhydride in excess to a temperature of 150°—160° for four or five hours, entirely dissolves and the solution, on cooling, deposits a large quantity of pale yellow scales; these are easily purified by draining off the excess of acetic anhydride, and recrystallising three or four times from glacial acetic acid. For the preparation of this compound, I find it is not necessary to use pure anthrapurpurin, the crude product before treatment with alcoholic caustic soda answering very well; but in this case the new compound should be recrystallised until the mother-liquors are of a clear pale yellow colour. The following analyses of this acetylic derivative were made:—

I. ·231 grm. of substance dried at 100° gave
·5328 „ „ CO_2, and
·0796 „ „ H_2O.

II. ·2563 grm. of substance dried at 160°—170° gave
·5899 „ „ CO_2, and
·0870 „ „ H_2O.

These numbers give percentages agreeing with those required for the formula—

$$C_{14}H_5(C_2H_3O)_3O_5 = C_{20}H_{14}O_8,$$

as the following comparisons show:—

	Theory.		Experiment. I.	Experiment. II.
C_{20}....	240	62·83	62·90	62·77
H_{14} ..	14	3·66	3·8	3·77
O_8....	128	33·51	—	—
	382	100·00		

Although the above numbers agree best with the formula of a triacetyl-compound, they also approximate closely to those required by a diacetyl-derivative, $C_{14}H_6(C_2H_3O)_2O_5 = C_{18}H_{12}O_7$, which would contain 63·5 p.c. of carbon and 3·5 p.c. of hydrogen. Therefore the only way to decide upon the nature of this substance was to decompose it and determine the weight of acetic acid or of anthrapurpurin which a given quantity would yield. Fortunately this acetylic product splits up readily under the influence of alcoholic potash or soda; this rendered the determination easy, especially as anthrapurpurin is nearly insoluble in cold water. The operation was conducted in the following manner:—

A weighed quantity of the acetylic derivative was placed in a flask, and boiled for some time with alcoholic soda, until the alcohol had been nearly all driven off; water was then added, and the purple solution boiled until quite free from alcohol; the anthrapurpurin was then precipitated with hydrochloric acid, and after standing for twenty-four hours, was filtered off, a weighed filter being used; it was then well washed with cold water, dried at 110°, and weighed. As the filtrate contained a small quantity of anthrapurpurin in solution, it was agitated with ether, and the ethereal solution evaporated in a weighed dish. From the united weights of the colouring matter on the filter and that extracted from the washings with ether, the results were calculated.

The following results were obtained:—

I. ·6338 of substance gave
·4222 of anthrapurpurin = 66·61 p.c.

II. ·6127 of substance gave
·4118 of anthrapurpurin = 67·21 p.c.

The decomposition of triacetyl-anthrapurpurin according to the following equation:—

$$\underset{\text{Triacetylanthrapurpurin.}}{C_{14}H_5(C_2H_3O)_3O_5} + 3H_2O = \underset{\text{Anthrapurpurin.}}{C_{14}H_8O_5} + \underset{\text{Acetic acid.}}{3C_2H_4O_2}$$

would yield 67·01 of anthrapurpurin, a number closely agreeing with experiment, whereas a diacetyl derivative similarly decomposed would give 75·3 p.c. This substance is therefore a triacetylanthrapurpurin.

The colouring matter obtained in one of the above determinations was analysed, and the results recorded in combustion XII.

Triacetylanthrapurpurin melts at 220°—222°. It is not very soluble in alcohol, but is moderately so in glacial acetic acid. It crystallises from this latter solvent in beautiful pale yellow glistening scales, as already mentioned; it decomposes when heated with alkalis.

When added gradually and in small quantities at a time to nitric acid, sp. gr. 1·5 triacetylanthrapurpurin dissolves without effervescence, forming a dark yellow solution; this on being slowly added to a large quantity of cold water, deposits a pale brown precipitate, which when collected and washed, dissolves in potash with a reddish purple colour. This solution does not appear to give any bands when viewed by the spectroscope, but a considerable absorption in the orange and violet. The addition of acid causes the colouring matter to separate as an orange precipitate.* This substance dyes alumina mordants of an orange colour, and weak iron ones of a reddish purple.

Anthrapurpurin and Benzoyl Chloride.

On boiling anthrapurpurin with benzoyl chloride, hydrochloric acid is evolved, and the colouring matter quickly dissolves. The resulting product when cold becomes a viscid mass, and is purified first by repeated boilings with water to decompose the excess of benzoyl chloride and remove a large quantity of the resulting benzoic acid, and then by crystallisation from glacial acetic acid. This latter operation requires to be repeated, and, after a portion of the substance which at first separates as a yellow powder has been filtered off, the mother-liquor, on being allowed to stand, gradually yields small groups of crystals of a dark yellow or brownish colour, in the form of rosettes.

* Diacetylalizarin, when treated in the same manner, yields a colouring matter, crystallising in needles from glacial acetic acid. It dyes alumina mordants a bright orange colour, and iron mordants of a very red purple. The colours are superior to those mentioned above. It dissolves in alkalies with a purple colour, and the solution gives a spectrum, showing a considerable absorption in the orange, which appears to consist of two indistinct bands. It does not appear to be Strecker's nitroxyalizarin, as that dissolves in alkalies with a red colour. (*Bull. Soc. Chem. d. Paris*, vol. xi, p. 260.)

These, when viewed under the microscope, appear well formed and transparent. This substance gave on analysis the following numbers:—

I. ·2756 of substance gave
·7438 of CO_2, and
·0893 of H_2O.

II. ·2527 of substance gave
·6826 of CO_2, and
·0822 of H_2O.

III. ·2410 of substance gave
·6515 of CO_2, and
·0800 of H_2O.

These numbers agree with those required by the formula—

$$C_{14}H_5(C_7H_5O)_3O_5 = C_{35}H_{20}O_8.$$

as the following comparisons show—

	Theory.				
C_{35}....	420	73·94	73·6	73·65	73·72
H_{20} ..	20	3·53	3·6	3·53	3·68
O_8....	128	22·53	—	—	—
	568	100·00			

The substance is therefore *tribenzoylanthrapurpurin.* A dibenzoyl derivative would require 72·5 p.c. of carbon, and 3·45 of hydrogen.

Tribenzoylanthrapurpurin fuses at 183°—185°. It is moderately soluble in boiling glacial acetic acid. Alcoholic potash decomposes it.

From the foregoing results it is evident that anthrapurpurin may be regarded as anthraquinone, in which three atoms of hydrogen are replaced by three molecules of HO. This substance and its two derivatives just described may be written thus—

$$C_{14}H_5O_2\begin{cases}HO\\HO\\HO.\end{cases} \qquad C_{14}H_5O_2\begin{cases}(C_2H_3O)O\\(C_2H_3O)O\\(C_2H_3O)O.\end{cases} \qquad C_{14}H_5O_2\begin{cases}(C_7H_5O)O\\(C_7H_5O)O\\(C_7H_5O)O.\end{cases}$$

Anthrapurpurin, or trioxyanthraquinone. Triacetylanthrapurpurin. Tribenzoylanthrapurpurin.

Other Compounds of Anthrapurpurin.

Anthrapurpurin forms metallic derivatives, most of which are insoluble or nearly so in water, except those of the alkali metals.

Solutions of potassic and sodic hydrate dissolve anthrapurpurin, producing beautiful violet-coloured liquids, which become blue in shade

when heated. They are not so blue as those obtained with alizarin. The sodium derivative is difficultly soluble in alcohol. Anthrapurpurin also dissolves in solutions of the alkaline carbonates with a reddish purple colour, from which it is precipitated by carbonic acid. A solution of sodic bicarbonate if gently heated, dissolves anthrapurpurin more readily than it does alizarin.

With the chlorides of calcium, magnesium, barium, and strontium, its ammoniacal solution gives purple precipitates. Specimens of the barium precipitate have been frequently examined after drying at 170°—180°, but the results have not been satisfactory, the percentage of barium being about 2 lower than that required by the formula, $C_{28}H_{10}Ba_3O_{10}$. With alumina it forms a red lake somewhat similar to that produced with purpurin.

Cupric acetate when added to an alcoholic solution of anthrapurpurin, changes it from yellow to a beautiful purple, which cannot be distinguished from that produced with alizarin under the same circumstances.

When boiled with alum or sulphate of alumina, it does not give any special reaction, whereas it will be remembered that its isomeride, purpurin, gives a pink solution which is fluorescent. In basic aluminic sulphate, however, it dissolves to some extent, forming an orange-pink solution, which is not fluorescent; acids precipitate the colouring matter from this

Anthrapurpurin and Ammonia.

When an ammoniacal solution of anthrapurpurin is heated to 100° in a sealed tube for some hours, its purple colour changes to indigo blue. This solution when acidified with hydrochloric acid deposits the new product as a dark purple precipitate, which dissolves in ammonia and in sodium carbonate with a blue colour, but in caustic alkalies with a red purple colour. It dyes alumina mordants purple, and weak iron mordants an indigo blue.

This product is probably isomeric with Dr. Stenhouse's purpurein or purpuramide.

Anthrapurpurin and Bromine.

A quantity of anthrapurpurin was digested with bromine and carbon disulphide for several hours in a flask connected with an inverted condenser. The excess of these substances was then driven off, and the residue crystallised from glacial acetic acid. The orange-coloured product was found to contain large quantities of bromine, and this when determined, gave a number a little higher than that required by the formula of dibromanthrapurpurin, $C_{14}H_6Br_2O_5$. I hope to examine this substance more fully.

Anthrapurpurin and Nitric Acid.

Ordinary nitric acid acts rapidly upon anthrapurpurin when heated, evolving a large quantity of red fumes. A few grams of a moderately fine specimen when treated with this acid was found to yield oxalic acid and a nitro-acid, but no phthalic acid

Absorption-spectra of Anthrapurpurin.

When the first specimens of this colouring matter were prepared, I was under the impression that they were not perfectly pure, but contained minute quantities of alizarin, as their solution in caustic potash always gave two absorption-bands in the same region of the spectrum as alkaline alizarin solutions do. But from a closer study of the processes used in the preparation of this body, and from the examination of specimens obtained from the perfectly pure acetylic derivative, I am convinced that these bands are due to anthrapurpurin itself. In solutions prepared with caustic alkalis, these absorption-bands are more decided than in those in which alkaline carbonates are used; in either case, however, they are much fainter than those of alizarin. The ammoniacal solution does not appear to give bands, nor does the ethereal solution of the colouring matter; in the latter case, however, the violet is almost entirely absorbed.

Anthrapurpurin as a Dyeing Agent.

This substance has about the same affinity for mordants as alizarin. The colours it produces are also analagous to some extent, as it produces red with alumina, purple and black with iron mordants.

There is, however, a considerable difference in the shade of colour produced, the reds being much purer and less blue than those of alizarin, whilst the purples are bluer and the blacks more intense. The fastness of the colours against soap and light are quite equal to those produced with alizarin.

When used to dye Turkey-red, it produces very brilliant colours of a scarlet shade, which are of remarkable permanence.

The patterns attached to this paper are only amateur productions; if dyed on the large scale the colours would probably be purer, but they serve to illustrate the difference between the shades of colour produced with anthrapurpurin and pure alizarin.

On some future occasion I hope to give an account of the reaction by which anthrapurpurin is formed in the manufacture of alizarin.

I am at present engaged in an endeavour to produce some new derivatives of the purpurin of madder containing acetyl, &c.

XVI.—*On Aurin.*

By R. S. Dale, B.A., and C. Schorlemmer, F.R.S.

Kolbe and Schmitt obtained in 1861 a red colouring matter by heating phenol with oxalic acid and concentrated sulphuric acid (*Ann. Chem. Pharm.*, 119, 169). Since that time this colour has been largely manufactured, and is found in commerce under the name of *aurin*, *yellow corallin*, or *rosolic acid*. The latter name, as is well known, was first given by Runge to a red body, which he obtained from coal-tar, and this name was afterwards employed to designate all red compounds which may be obtained from phenol by different reactions.

We refrain from giving a historical sketch of these red phenol-colours, because there cannot be any doubt that, according to the mode of preparation, different compounds are formed.

In two preliminary notes (this Journal [2], ix, 466; *Proc. Lit. Phil. Soc.*, xi, 12, and this Journal [2], x, 74) we have already stated that we have succeeded in isolating the pure colouring matter from the commercial product. Soon after our first publication, H. Fresenius published a short paper, in which he stated that he was also engaged with an investigation of this body (*Journ. prakt. Chem.* [2], iii, 477), and afterwards he described more fully the red compound which he obtained by heating a mixture of one part of crystallised oxalic acid, one part and a half of colourless, crystallised phenol, and two parts of sulphuric acid to 140°—150° for 5—6 hours (*Journ. prakt. Chem.* [2], v, 184, and this Journal [2], x, 705). The analysis of the crystallised body, which Fresenius calls *corallin*, gave numbers agreeing with the formula $C_{40}H_{38}O_{11}$. We shall have to refer to Fresenius's paper again, and will only for the present mention that his corallin is not identical with the compound, which we have obtained, and for which we retain the name of *aurin*.

Commercial aurin is a brittle, resinous body, having a beetle-green lustre, and yielding a red powder. The material used for this investigation was put at our disposal with great liberality by Messrs. Roberts, Dale and Co., Cornbrook, Manchester, who also gave us leave to purify the crude product in their works.

This purification is easily effected by adding concentrated aqueous, or better, alcoholic ammonia, to a cold, concentrated, alcoholic solution of crude aurin. A crystalline precipitate, a compound of aurin with ammonia, separates out, whilst the other bodies contained in the crude product, remain in solution. The ammonia-compound was washed with alcohol by means of the filter-pump; after drying, it forms a dark red

crystalline powder with a bluish lustre. It is a very unstable body, losing its ammonia completely when it is exposed to the air for some time.

By boiling it with dilute acetic acid or hydrochloric acid, aurin is obtained as a crystalline, brownish-red powder, having a green lustre; it must be purified by repeated crystallisation from acetic acid.

By the first crystallisation it was generally obtained in small, dark red needles, with a steel-blue reflection; afterwards it crystallised in larger needles or prisms, having the colour of chromic acid and a brilliant diamond lustre, or of a darker shade showing a blue or greenish-blue reflection, and once we obtained it in small crystals, having the beetle-green lustre of the salts of rosaniline.

The finest crystals were formed by the spontaneous evaporation of an alcoholic solution containing acetic acid. We have analysed these different specimens partly dried at 100° and partly at a higher temperature, and although samples of the same preparation gave very concordant results, those of different preparations varied very much in their composition. We found that the reason for this was that aurin most obstinately retains water and acetic acid, which, however, as we believe, are not chemically combined with it.

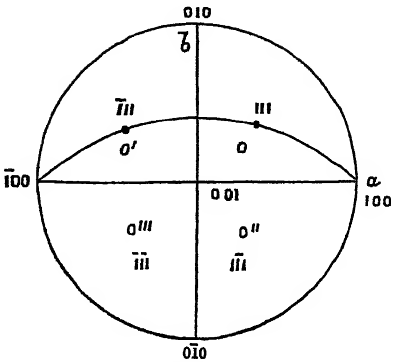
From hot concentrated hydrochloric acid, aurin crystallises in slender red needles, which, when dried at 110°, still retain a large quantity of hydrochloric acid. We tried to obtain the pure compound by precipitating a dilute alkaline solution of aurin with weak hydrochloric acid and washing the precipitate with the filter-pump, but the product thus obtained also contained hydrochloric acid when dried at 110°.

By the spontaneous evaporation of an alcoholic solution, aurin is obtained in dull red crystals with a green lustre, which when dried at 110° do not contain any alcohol, but several per cent. of water, which is given off only at a temperature above 140°.

Aurin, which has been repeatedly crystallised from acetic acid or alcohol, does not melt at 220°; at this temperature the crystals assume a darker shade, which disappears again on cooling, without any appearance of alteration in the substance. When more strongly heated, it melts, emitting at the same time the odour of phenol, and solidifies again on cooling to an amorphous, beetle-green mass. Aurin dissolves readily in alkalis with a magenta-red colour, and is precipitated from this solution by acids as a crystalline powder.

Our best thanks are due to Mr. W. J. Lewis of Oriel College, Oxford, who examined the crystals, and communicated to us the following results:—

Aurin, crystallised from a mixture of alcohol and acetic acid, forms dark red crystals, moderately thick in comparison to length.



Crystals, trimetric; ratio of axes:
1 : 0·5604 : 0·4719

Forms, 100, 010, 111
$\surd$ 00′ = 37° 38′
$\surd$ 00″ = 91° 20′

Face *b* has a strong steel-blue reflection, and seems irregular and conchoïdal in fracture. 001 is not present. No good sections could be obtained for determining the plane of the optic axes. It seemed however to be perpendicular to the planes 100 and 010, and therefore parallel to 001.

The red crystals from acetic acid have the same form, but are not so thick in comparison with the length.

We have already mentioned that aurin crystallised from acetic acid is not fit for analysis; even after it has been heated for some time to 220° it gives off the odour of acetic acid, when heated to the melting point, at which temperature it already begins to decompose, as is shown by the odour of phenol becoming perceptible at the same time. Two analyses of a product which had been crystallised five times from acetic acid and heated for two days to 220° gave—

$$C = 77·87 \text{ and } 77·95 \text{ and } H = 5·04 \text{ and } 5·09.$$

After recrystallising it once from alcohol, it gave numbers (analysis 4) agreeing with those obtained by the analyses of samples which had several times been crystallised from alcohol (Nos. 1, 2, and 3), and that of the large crystals, obtained from a mixture of alcohol and acetic acid (No. 5).

As aurin when heated leaves a large quantity of difficultly combustible carbon, all combustions were finished in a current of pure oxygen—

	Substance.	CO_2.	H_2O.
(1.)	0·3620	1·0590	0·1710
(2.)	0·3465	1·0095	0·1665
(3.)	0·3270	0·9510	0·1485
(4.)	0·2970	0·8715	0·1365
(5.)	0·2135	0·6270	0·0980

	(1.)	(2.)	(3.)	(4.)	(5.)
C	79·78	79·45	79·32	80·03	80·09
H	5·24	5·34	5·04	5·10	5·10

The formula $C_{21}H_{16}O_3$ agrees best with the results of the analysis, whilst the formula $C_{20}H_{14}O_3$ which we adopted in our second preliminary note requires less carbon and hydrogen:—

	Calculated for		Mean found.
	$C_{21}H_{16}O_3$.	$C_{20}H_{14}O_3$.	
C	79·75	79·47	79·73
H	5·06	4·63	5·16
O	15·19	15·90	15·11
	100·00	100·00	100·00

For reasons which we shall state further on, we believe, however, that the second formula is more probable than the first. As the different compounds and derivatives of aurin obtained by us are not well suited for an exact determination of its molecular weight, from which the correct formula might be deduced, we shall give in this paper the percentage composition calculated for both formulæ.

Compound of Aurin and Sulphur Dioxide.—When sulphur dioxide is passed into a hot concentrated alcoholic solution of aurin, the dark yellowish-red liquid assumes a lighter colour, and on cooling a compound of aurin and sulphur dioxide separates out, forming either brick-red crystalline crusts or granular garnet-red crystals, having a more or less beetle-green lustre. The compound dried over sulphuric acid does not retain any alcohol, but a considerable quantity of water, which is not expelled at 100°; but above this temperature it is given off, together with sulphur dioxide.

The determination of aurin and sulphur dioxide gave the following results:—

(1.) Brick-red crusts, dried at 100°, 0·6516, were fused with nitre and sodium carbonate, and gave 0·2075 $BaSO_4$.

(2.) Garnet-red crystals, dried over sulphuric acid; 0·4368 treated in the same way gave 0·1365 $BaSO_4$.

(3.) Crystals with a strong beetle-green lustre, dried over sulphuric acid; 0·2560 oxidised with potassium chlorate and hydrochloric acid gave 0·0765 $BaSO_4$.

(4.) 0·8175 of the garnet-red crystals left after heating to 180° 0·6460 aurin.

(5.) 0·3662 of brick-red crusts left 0·2899 aurin.

(6.) 0·3312 of the same preparation gave 0·2620 aurin.

	(1.)	(2.)	(3.)	(4.)	(5.)	(6.)
SO_2	8·75	8·55	8·20	—	—	—
Aurin	—	—	—	79·02	79·16	79·10

These numbers show that the compound contains one molecule of sulphur dioxide combined with two molecules of aurin. Whether the water existing in it is chemically combined or adheres to it only mechanically, as is the case with aurin, cannot as yet be decided. Assuming the water to be in combination, the following two formulæ may represent the compound:—

	Calculated for		
	$(C_{21}H_{16}O_3)_2SO_2 + 5\frac{1}{2}H_2O$;	$(C_{20}H_{14}O_3)_2SO_2 + 5\frac{1}{2}H_2O$.	Mean found.
Aurin....	79·49	78 74	79·09
SO_2	8·05	8·34	8·50
H_2O	12·46	12·92	12·41
	100·00	100·00	100·00

Aurin-potassium Bisulphite is produced by adding a solution of potassium bisulphite to a hot concentrated, alcoholic solution of aurin, until the yellowish-red colour of the latter has disappeared. A soft white powder resembling precipitated chalk separates out, the quantity of which increases when the solution is allowed to stand. Under the microscope, it has quite a uniform appearance, consisting of small rectangular plates. It is more soluble in water than in alcohol, and may be recrystallised from hot water, but on boiling the aqueous solution, decomposition sets in and aurin is precipitated. Acids as well as alkalis decompose it readily, so that on exposure to the air, it soon assumes a yellow or reddish tint.

(1.) 1·1350 gave 0·2340 K_2SO_4.
(2.) 0·8800 gave 0·1770 K_2SO_4.
(3.) 0·4930 gave 0·2750 $BaSO_4$.
(4.) 0.7005 gave 0·3705 $BaSO_4$.

	Calculated for		Found.			
	$C_{21}H_{16}O_3 + KHSO_3$;	$C_{20}H_{14}O_3 + KHSO_3$.	(1.)	(2.)	(3.)	(4.)
K....	8·95	9·26	9·25	9·02	—	—
S....	7·34	7·58	—	—	7·64	7·26

Aurin-ammonium Bisulphite is obtained by a reaction similar to that which yields the potassium compound, to which it has the greatest resemblance. Its analysis was conducted as follows: the compound was evaporated to dryness with an excess of dilute hydrochloric acid; the residue dried at 180°, after cooling, the ammonium chloride was washed out with a small quantity of cold water; and the residual aurin was again dried at 180° and weighed.

(1.) 0·7565 gave 0·5625 aurin, and 0·1800 metallic platinum.
(2.) 0·5275 gave 0·3030 $PtCl_4 + 2NH_4Cl$.

	Calculated for		Found.	
	$C_{21}H_{16}O_3 + (NH_4)HSO_3$;	$C_{20}H_{14}O_3 + (NH_4)HSO_3$.	(1.)	(2.)
Aurin .	76·14	75·31	74·36	—
NH_3 ..	4·09	4·24	4·09	4·37

Aurin-sodium Bisulphite has properties very similar to those of the two preceding compounds, but appears to be more soluble in water.*
1·5695 gave 1·1570 aurin and 0·2470NaCl.

	Calculated for		Found.
	$C_{21}H_{16}O_3 + NaHSO_3$;	$C_{20}H_{14}O_3 + NaHSO_3$.	
Aurin..	75·24	74·38	73·72
Na	5·48	5·66	6·19

Leucaurin.—Kolbe and Schmitt found that their red compound yielded, on treatment with acetic acid and iron filings, a colourless body soluble in alkalis. On exposing this solution to the air, it gradually assumed a red colour, and on adding potassium ferricyanide, an intensely red liquid is formed at once. The alkaline solution of the red body also becomes colourless in contact with sodium-amalgam, but turns red again on exposure to the air.

We prepared our leucaurin either by heating an alkaline solution of aurin with zinc-dust and precipitating the colourless liquid with hydrochloric acid, or by acting with zinc-dust on a solution of aurin in acetic acid, or on an acidulated alcoholic solution. On diluting the colourless liquid with water, leucaurin separates as a crystalline precipitate, and from the mother-liquor a further quantity crystallises out in needles on standing.

Pure leucaurin is perfectly colourless; but when recrystallised it readily assumes a yellowish tint. It is freely soluble in acetic acid, crystallising therefrom in thick and tolerably hard prisms, the faces of which are developed at one extremity only, whilst the other extremity is very irregular; it also shows a strong tendency to twin. From an alcoholic solution it was obtained in extremely friable prisms. It may be heated to 130° without melting, assuming, at the same time, a

* When we first prepared this body we used dilute solutions containing an excess of sodium bisulphite; on standing, large prisms crystallised out, which we believed to be the new compound, but analysis showed that they were nothing but sodium bisulphite enclosing some mother-liquor. On concentrating the remaining solution, a mass of silky needles crystallised out, which could not be freed completely from the syrupy mother-liquor. Analysis gave numbers agreeing with those required by a compound containing two molecules of sodium bisulphite, one molecule of aurin, and water of crystallisation.

reddish colour; on heating it more strongly, it gradually softens and assumes a deep red colour. Its alkaline solution readily absorbs oxygen, and becomes of a dark red colour on the addition of potassium ferricyanide. The red compound thus produced is, however, not aurin, but probably an oxidation-product of that body; on adding an acid to the solution, a brown precipitate is formed, which is almost insoluble in alcohol and acetic acid.

The analysis of leucaurin gave the following numbers:—

	Substance.	CO_2.	H_2O.
(1.)	0·3168	0·9150	0·1660
(2.)	0·3471	1·0080	0·1850
(3.)	0·2970	0·8580	0·1680
(4.)	0·2375	0·6842	0·1285
(5.)	0·2427	0·7020	0·1270

	(1.)	(2.)	(3.)	(4.)	(5.)
C....	78·77	79·20	78·78	78·56	78·89
H....	5·85	5·92	6·09	6·00	5·81

	Calculated for		Mean found.
	$C_{21}H_{18}O_3$;	$C_{20}H_{16}O_3$.	
C.......	79·25	78·94	78·84
H.......	5·66	5·26	5·93
O.......	15·09	15·80	—
	100·00	100·00	

Leucaurin contains three hydroxyls, the hydrogen of which can be easily replaced by acid radicals.

Triacetyl-leucaurin is produced by heating leucaurin with an excess of acetyl chloride. As this compound is readily decomposed by alkalis and by boiling water, which converts it into a resinous body, the product of the reaction must be purified by shaking it well with cold water and crystallising the body from warm alcohol. It is readily soluble in alcohol and acetic acid, and forms short silky needles.

The substance used for analysis was dried over sulphuric acid.

(1) 0·3120 gave 0·8385 CO_2 and 0·1580 H_2O
(2) 0·2925 gave 0·7875 CO_2 and 0·1545 H_2O

	Calculated for		Found.	
	$C_{21}H_{15}O_3(C_2H_3O)_3$;	$C_{20}H_{13}O_3(C_2H_3O)_3$.	(1.)	(2.)
C	72·98	72·56	73·29	73·42
H	5·41	5·12	5·62	5·88
O	21·61	22·32	—	—
	100·00	100·00		

Tribenzoyl-leucaurin is readily formed when leucaurin is heated with benzoyl chloride. It is a very stable body, which is not acted upon by boiling it with weak caustic soda, and may be heated to 180°, and even higher, without decomposition. It is but sparingly soluble in alcohol and acetic acid, but freely in benzene, from which it separates in transparent crystals containing benzene, which they lose when exposed to the air or when heated, the crystals falling to powder. The substance used for analysis was dried at 180°.

(1) 0·2195 gave 0·6465 CO_2 and 0·0965 H_2O
(2) 0·2290 gave 0·6735 CO_2 and 0·1035 H_2O

	Calculated for		Found.	
	$C_{21}H_{15}O_3(C_7H_5O)_3$;	$C_{20}H_{13}O_3(C_7H_5O)_3$.	(1.)	(2.)
C	80·00	79·87	80·32	80·21
H	4·76	4·55	4·88	5·02
O	15·24	15·58	—	—
	100·00	100·00		

Although we have, so far, not succeeded in establishing definitely the formula of aurin, there can be hardly any doubt that this body is not identical with Fresenius's corallin, which melts already at 156°, and crystallises in combinations of prisms and pinacoïd planes, whilst aurin does not melt even at 220°, and contains only pinacoïds and octoïds, which latter are not to be found in corallin; moreover, the axial parameters of the two kinds of crystals, which both belong to the trimetric system, are very different.

It appeared to us of interest to discover the cause of this difference, and we therefore prepared the colouring matter from pure phenol, boiling quite constantly at 184° and melting at 42°, a large quantity of which was kindly placed at our disposal by Messrs. Chas. Lowe and Co. Some preliminary experiments showed that the formation of the colour begins already between 100°—110°; we have, therefore, heated the mixture not above this temperature, in order to avoid, as much as possible, the formation of bye-products, in which we have quite succeeded. After heating for five or six days, a sufficient quantity of colour was produced, which was precipitated by water and boiled to remove free phenol. The resinous substance showed, after cooling, a crystalline fracture. To get rid of the phenol still adhering to it, the compound was dissolved in dilute caustic soda, and reprecipitated by weak hydrochloric acid. A crystalline precipitate was obtained, which crystallised from alcohol completely in small but distinct needles, having the colour of chromic trioxide and a diamond lustre, and capable of bearing a heat of 220° without undergoing any change. Mr. Lewis

has also examined this compound, and found that it gave the same result as that crystallised from a mixture of alcohol and acetic acid; only the steel-blue reflection on face 010 was not perceived. It is rather remarkable that aurin prepared from pure phenol does not retain water in the same way as that obtained from the commercial product; the substance dried over sulphuric acid is anhydrous, no loss of weight taking place on heating it to 200°. From dilute alcohol we once obtained needles which had a green lustre, and on drying at 100° fell to powder, and therefore probably contained water of crystallisation. To our regret we did not succeed in obtaining them again.

The results of the analysis are as follows:—

	Substance.	CO_2	H_2O.
(1.)	0·2657	0·7755	0·1218
(2.)	0·5260	1·5280	0·2350
(3.)	0·3268	0·9525	0·1470
(4.)	0·2980	0·8645	0·1385

	(1.)	(2.)	(3.)	(4.)
C	79·60	79·22	79·49	79·12
H	5·09	4·94	5·00	5·16

These numbers agree with those required by the formula $C_{20}H_{14}O_3$:

	Calculated.	Found, mean.
C......	79·47	79·38
H	4·63	5·05
O......	15·90	—

By heating this compound with acetic acid and zinc-dust, we obtained the leuco-compound, crystallising from alcohol in brilliant white needles, which were dried over sulphuric acid and analysed:

	Substance.	CO_2.	H_2O.
(1.)	0·2340	0·6725	0·1220
(2.)	0·3058	0·8773	0·1575
(3.)	0·2210	0·6373	0·1165

	(1.)	(2.)	(3.)
C	78·33	78·24	78·64
H	5·80	5·72	5·85

These numbers agree better with the formula $C_{20}H_{18}O_3$, than with $C_{20}H_{16}O_3$:

	Calculated for		Mean found.
	$C_{20}H_{16}O_3$;	$C_{20}H_{18}O_3$.	
C	78·94	78·43	78·42
H	5·26	5·88	5·79
O	15·80	15·69	—
	100·00	100·00	

But as most of these bodies retain water so obstinately, and as, in order to avoid oxidation, the compound was only dried over sulphuric acid, the formula $C_{20}H_{16}O_3$ is the more probable.

The aurin from pure phenol is, if not identical with that contained in the commercial product, certainly very nearly related to it, and consequently different from Fresenius's corallin. The cause of this difference must be looked for in the different modes of preparation. Fresenius, as well as Kolbe and Schmitt, prepared their compound by heating the mixture to 140°—150°, whilst our body was formed at a temperature not exceeding 110°.

The aurin from pure phenol being obtained without the formation of bye-products, the reaction by which it is formed may be expressed by the following equation:

$$3C_6H_6O + 2CO = C_{20}H_{14}O_3 + 2H_2O.$$

The phenol used for the preparation of the commercial product always contains a small quantity of cresol, and it appears probable that the latter takes part in the reaction, which might take place as follows:

$$2C_6H_6O + C_7H_8O + 2CO = C_{21}H_{16}O_3 + 2H_2O.$$

In order to elucidate this point, we have made the following experiments:—

Aurin from the commercial product was well mixed with zinc-dust, the mixture gradually heated in a combustion-tube, and the products of decomposition passed over a long layer of red-hot zinc-dust. The yield of hydrocarbons thus formed was but small; the principal portion consisted of benzene boiling at 82°—85°; after it had passed over, the boiling point rose rapidly above 200°, and then more gradually to above 300°. The small fraction boiling between 85° and 200°, yielded by further distillation a little more benzene and bodies boiling above 200°, but no toluene could be found in it. The high-boiling fraction is a mixture of liquid and solid hydrocarbons, the quantity for the present at our disposal being, however, too small to effect a separation.

When aurin is heated carefully in a combustion-tube, a reddish-coloured oily liquid distils and a large quantity of porous carbon is formed. The distillate is almost completely soluble in caustic potash, only a trace of a solid having the odour of diphenyl being left behind. The alkaline solution was decomposed with hydrochloric acid, and the oil dried over calcium chloride. On distilling it, a small quantity of water first passed over, and the boiling point then rose rapidly to 184°, remaining constant until the last drop had distilled over; the distillate solidified to a mass of needle-shaped crystals, and consisted of pure

phenol, no cresol being present, the formation of which might have been expected if this compound took part in the production of the colour.

We may therefore, for the present, assume that the aurin contained in the commercial product is identical with that obtained from pure phenol. It is known how easily one may be deceived by the apparent purity of crystallised colouring matters; only a short time ago, Wichelhaus has again called attention to this point in his beautiful researches on the oxidation of phenol (*Deut Chem. Ges. Ber.*, v, 846). We hope to settle this question by further researches.

When aurin is heated with aqueous ammonia to 140°—150°, a new colouring is formed, dyeing on wool and silk a redder shade than aurin, and occurring in commerce under the name of "red corallin" or "pæonin." We have commenced an investigation of this body, the results of which are, however, not completed.

Another derivative of aurin, called "azurin" or "azulin," is produced by treating it with aniline. An examination of this blue compound has so far yielded the following results.

When aurin is gently boiled with aniline and a little acetic acid, the solution soon assumes a pure blue colour. On boiling the product with dilute hydrochloric acid, in order to remove an excess of aniline, a blue resinous substance is obtained, consisting of a mixture of different bodies, which are partly soluble in alcohol and acetic acid, and partly insoluble in them.

By heating the above mixture on a water-bath, a blue solution is formed in 16—20 hours, which, however, also contains several bodies. A portion of the product is readily soluble in caustic soda with a purple colour, and precipitated by acid from this solution in blue flakes, which dissolve in alcohol and acetic acid. The portion which is insoluble in alkalis dissolves completely in acetic acid and alcohol, with a fine blue colour, but ether takes up only a part of it, forming a dark red solution, which on evaporation leaves a blue resinous body behind. The portion not dissolving in ether forms a dark blue powder with a golden reflection.

We have not analysed any of these products, because we have not yet obtained them in distinct crystals.

XVII.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies.*

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

I. *On Iodide of Ethyl.*

LAST spring we read before the Royal Society a paper in which it was shown that zinc on which copper had been deposited is capable of decomposing water at the ordinary temperature, and at the close of that communication we mentioned that ethyl iodide may easily be decomposed by the same agent (*Proc. Roy. Soc.*, xx, 218).

We propose now to lay before the Chemical Society a description of the reactions of these conjoined metals with this organic body, following the course of the classic memoir of Frankland published in our Quarterly Journal for 1849 (vol. ii, p. 263). The difference between our method and his consists in the fact that while he, using zinc alone, had to confine the ingredients in closed vessels and expose them to a considerable heat, we, using zinc covered with spongy copper, make our experiments with ordinary flasks and delivery-tubes without artificial pressure.

Preliminary Experiments with Zinc.

In order to estimate the value of conjoining copper with zinc in these experiments, it was necessary to make a preliminary trial with zinc alone.

A flask having a capacity of about one ounce (29 c.c.) was filled with zinc foil, about the thickness of writing paper, 14 inches (35 centim.) long and 2 inches (5 centim.) wide, crumpled. To remove any trace of grease this was washed with alcohol, then with ether, and afterwards dried by heating in a current of dry carbonic acid gas.

Five c.c. or 9·5 grams of ethyl iodide were poured into the flask, a long inverted condenser was affixed to it by a perforated cork, and it was placed in a water-bath and heated to the boiling point of the iodide.

This was suffered to continue for an hour, the vapour condensing in the tube and dropping down again upon the metal. On pouring the ethyl iodide into water and shaking it up well, a trace of zinc oxide separated. This existence of a very small amount of action was attributed to those traces of impurity which are always found in zinc.

We repeated the experiment with zinc foil which had been deeply etched by sulphuric acid, since Petal has proposed that the metal in this condition should be used in the production of zinc-ethyl. We

found in the flask a small quantity of a white body soluble in ether, which when poured into water gave 0·04 grm. of zinc oxide. The increase of action was attributed to the etching having brought the impurities of the zinc into greater prominence; but the result was still insignificant in amount.

Action of the Dry Couple on Ethyl Iodide.

An experiment precisely similar to the above in other respects was tried with our couple. The *couple*, for so we shall now designate the zinc with its covering of spongy copper, was prepared by pouring a solution of cupric sulphate containing about 1·5 per cent. of the salt, on to the crumpled zinc foil in the flask, allowing it to deposit the finely divided metallic copper till it loses its blue colour, and repeating this two or three times. We find that a weak solution gives a more effective couple than when a strong one is used. The coating ought to adhere firmly, and present somewhat the appearance of black velvet. The whole must be well washed, first with water, then with alcohol, and lastly with ether, and thoroughly dried by heating it in a current of dry carbonic acid gas.

When ethyl iodide is added to this couple at the ordinary temperature there is little or no sign of action, but upon heating it in the water-bath, some combustible gas is given off, and a large amount of a crystalline body is produced. This has the appearance of Frankland's ethiodide of zinc, and when heated gently by itself, is resolved into zinc-ethyl and zinc iodide.

In order to estimate the amount of zinc-ethyl that may be produced, the following method was employed. The flask was immersed in a bath of boiling water; vapour of ethyl iodide immediately rose in the inverted condenser, but as the liquid fell back it could be seen to diminish, and when this action ceased, the first part of the operation was over. The condenser was then removed, and the flask was fitted with two tubes, one in connection with a carbonic acid generator, and the other bent down so as to dip under a stratum of mercury in a vessel into which water was afterwards poured. Carbonic acid was allowed gently to flow, the white crystalline body was gently heated by a gas flame, and the zinc-ethyl thus produced was swept through the second tube and through the mercury into the water, where, of course, it was decomposed. The oxide of zinc produced was dissolved in dilute hydrochloric acid, precipitated by sodium carbonate and weighed. The results were as follows:—

	C_2H_5I used.	Duration of first operation.	ZnO obtained.	Equivalent to $C_4H_{10}Zn$.
A............	9·5 grams.	15 min.	1·523	2·31
B............	"	30 "	1·316	2·04
C............	"	45 "	1·208	1·83
D............	"	25 "	1·348	2·04
E............	"	26 "	1·728	2·61

The experiments marked A, D, and E, were made at the ordinary pressure, and they afforded the best result both as to yield of zinc-ethyl and quickness of action. The experiments B and C were made at a pressure of from one to two inches of mercury; and in C, where the experiment took the longest time and yielded the lowest result, the amount of gas evolved was found to be 120 c.c. As the greatest possible amount of zinc-ethyl theoretically producible from 9·5 grm. of the iodide is 3·74 grm., it is evident that by our method the bulk of the iodide is converted into ethiodide of zinc, and it is evident also that zinc-ethyl might be prepared in this manner on a large scale.

As it has been recommended to mix ether with the iodide in the preparation of zinc-ethyl, we thought it desirable to see whether it offered any advantage in our mode of operation. An experiment was made as before, except that 5 c.c. of anhydrous ether were added; but though the heat was continued for half an hour, the oxide of zinc obtained was only 0·94 grm., equivalent to 1·43 grm. of zinc-ethyl. The ether therefore appears to retard the action.

Thinking that less gas and therefore more ethiodide would be produced at a lower temperature, we made experiments which showed it was possible to effect the chemical change at 50° C.; but at that temperature it is some time, perhaps half an hour, before the action commences, and it is difficult to know when the whole of the iodide is converted. It is therefore necessary to raise the heat somewhat, especially toward the end of the experiment. In an operation conducted in this manner, with every precaution to ensure the greatest yield; the zinc oxide indicated 2·5 grm. of zinc-ethyl, which barely equals that of experiment E, and is only two-thirds of the quantity theoretically possible. We could not account for the loss of this 33 per cent., unless by supposing that when the crystalline body is heated, other substances are produced besides zinc-ethyl and zinc iodide.

Another experiment was therefore made, in which the usual amounts of substances were heated together in a water-bath, first at 50°, and afterwards to about 85°. The flask was then attached to a delivery-tube passing into a small receiver, from which another tube passed into a vessel of mercury. The apparatus was filled with dry carbonic acid gas, and the crystalline body was gently heated. It became

entirely liquid before the thermometer indicated 75°, and at a higher temperature it rather suddenly gave off the zinc-ethyl, which condensed easily in the first tube and ran down into the receiver, while there passed on a considerable quantity of combustible gas. A portion of this was collected, and after the separation of a little carbonic anhydride, Nordhausen sulphuric acid absorbed nearly half the remainder, leaving a residual gas that burnt with a luminous flame. It was evident therefore that a good deal of the crystalline body suffered a decomposition which yielded gases of two types, probably ethylene and ethyl hydride in equal volumes. A small amount of a bluish black substance was formed in the flask.

Frankland considered that the ethylene and ethyl hydride found among the products of the action of zinc upon the iodide in sealed tubes, are due to the action of ethyl iodide on the ethiodide of zinc; it was thought that by heating our couple with an excess of the iodide, direct evidence of this reaction might be obtained.

3·15 grms. of the couple and 19 grms. of ethyl iodide were therefore heated together for two hours. A few bubbles of gas were given off during the first few minutes. In the flask there remained the spongy copper and a little of the couple unacted on, which were separated from the solution of ethiodide of zinc in ethyl iodide by filtration through asbestos. This liquid was again heated for an hour and a half; only about 10 c.c. of gas were evolved, and that during the earlier part of the time. On heating it in a water-bath, ethyl iodide distilled over; on raising the temperature, the same iodide mixed with zinc-ethyl passed over, and afterwards zinc-ethyl apparently pure. It appears therefore, that whatever may be the case in sealed tubes, ethiodide of zinc is not decomposed by ethyl iodide at a temperature of 70°, and at the ordinary atmospheric pressure.

The question naturally arises, What is the manner in which the couple has acted on the ethyl iodide? The main result is, the crystalline body. This has been viewed in two ways: either as a direct combination of the iodide with the metal $C_2H_5I.Zn$; or as a combination of the zinc-ethyl and zinc iodide $(C_2H_5)_2Zn.ZnI_2$, which are produced by the splitting up of the iodide by means of the metal.

We are inclined to the latter view because, first, the splitting up of a binary compound seems the more especial function of a couple; secondly, there is always found some zinc-ethyl mixed with the crystalline body, even when the temperature has been kept at the lowest; and thirdly, distilled zinc-ethyl will combine with dry zinc iodide, even without the application of heat, giving rise to a crystalline body which resembles in appearance that in the flask, and melts at about the same temperature.

Action of the Couple on Ethyl Iodide and Water.

It was shown by Frankland that if water be present when ethyl-iodide is heated with zinc under pressure, the water also suffers decomposition, and hydride of ethyl is produced in quantity. Now as our couple is able to decompose water at the ordinary temperature, we expected that the reaction just described would take place by means of it without any artificial heat. We were not disappointed.

Five c.c. of ethyl iodide were placed in an ounce flask containing the couple, which had been washed with water, and drained, but not dried. The temperature of the room was only 14°. Evolution of gas took place at once, and it was collected over water in the usual way. About twelve bubbles were given off per minute; then the action slackened, but the rate could be immediately increased by shaking the flask. After 32 hours no more gas was evolved, and the total amounted to 1255 c.c. (corrected for temperature and pressure).

This gas burned with a luminous flame, and was almost wholly soluble in recently boiled alcohol. A portion of it was passed through a set of bulbs containing respectively alcohol and water, and analysed according to Bunsen's method. Nordhausen sulphuric acid caused no diminution of volume.

After removal to the eudiometer the following were the data obtained:—

	Observed vol.	Temperature.	Difference of Hg level.	Barometer.	Vol. at 0° C. and 1 m.
Gas used (moist)	18	16·0°	155	755·14	6·58
After adding air and O (moist)	283	16·8°	188	755·47	152·66
After combustion (moist)	262	16·2°	209	755·92	136·86
After absorption of CO_2 (dry)	236	9·3°	235·2	759·2	124·07

giving the following results as compared with those calculated for hydride of ethyl.

	Found.	C_2H_6.
Gas burnt	6·58	—
Contraction	15·8	16·45
Carbonic anhydride	12·79	13·16

This, taken in conjunction with its physical properties, confirms the belief that this gas was hydride of ethyl, but mixed probably with a small amount of free hydrogen arising from the action of the couple on the water alone.

The 1255 c.c. of gas collected, making allowance for loss by the

carrying over of iodide vapour, and absorption by water, fairly represents the total amount which could be obtained theoretically, viz., 1365 c.c.

The residue in the flask had a faint odour, suggesting that of acetic ether. There was a white substance adhering to the undestroyed couple. On distillation some water passed over with a trace of an ethereal body, but no iodide of ethyl. From what was left, alcohol dissolved out zinc iodide, leaving the hydrate.

Action of the Couple on Ethyl Iodide and Alcohol.

The substitution of alcohol for water in the above reaction makes little change, though the couple was found to have no effect whatever upon absolute alcohol itself, even at a boiling temperature. The evolution of gas commences at a few minutes after the substances have been placed together, if the temperature be 20°; but if it be lower, a quarter or half an hour is required to start the action; but when it is once fairly started, the temperature rises, and the decomposition proceeds rapidly.

In one experiment 5 c.c. of ethyl iodide were poured on to the couple which had been washed with alcohol but not dried. The action was moderated by immersing the flask in water, at about 19°. The amount of gas obtained was, after correction, 1170·7 c.c.

In another experiment 5 c.c. of ethyl iodide were mixed with 10 c.c. of absolute alcohol, and poured upon the dry couple. The action was allowed to take its natural course, and in 15 minutes after it had begun, 1060 c.c. of gas were collected. The whole evolved amounted to 1114 c.c.

On repeating the latter experiment, using 5 c.c. of alcohol, the gas collected was 1101 c.c.

It would appear therefore that the yield of gas is not quite equal to what is obtained by the agency of water instead of alcohol, and of course it does not approach so nearly the theoretical amount of 1365 c.c.

The gas had the same properties as before, and was analysed in the same way. Sulphuric acid did not alter its volume, at least not beyond the extent of possible errors of observation.

Two combustions were made.

	Volume observed.	Temperature.	Difference of Hg level	Barometer.	Vol. at 0° C. and 1 m.
			mm.		
I. Gas used (moist)....	21	17·1	419	758 95	7·882
After adding air and O (moist)..	293	16·6	173·5	757 39	162 25
After combustion (moist)........	269	17·1	198·5	756·61	142·51
After absorption of CO_2 (dry)......	244	17 1	223 5	756·38	126·87
II. Gas used (moist)....	16·5	16·6	153·0	758·1	6·239
After adding air and O (moist)..	261·3	16·6	205·9	758·1	137 17
After combustion (moist)........	240 5	16 6	226·5	758·1	121 55
After absorption of CO_2 (dry)	217·8	17·7	250 2	762·5	109·19

These numbers give the following results:—

	I.		II.	
	Found.	Calculated.	Found.	Calculated.
Gas employed	7 88	—	6·24	—
Contraction	19 74	19 70	15·62	15·60
Carbonic anhydride......	15·64	15·76	12·3	12 48

It appears therefore that the gas is pure ethyl hydride.

In Frankland's experiment, where the substance had been exposed to a high temperature and to pressure, he had reason to believe that the residue contained oxyiodide of zinc and ether. We could never detect the least odour of this latter substance either in the flask or in the bulbs through which the gas had bubbled. The residue in our case was a substance of a gummy consistency, in which some beautiful prismatic crystals were once observed; it dissolves completely in absolute alcohol, and from this alcoholic extract water throws down a bulky precipitate of zinc hydrate. A certain measure of this alcoholic solution gave on analysis 0·694 grm. of silver iodide, and 0·230 grm. of zinc oxide, of which 0·104 grm. was precipitable by water.

This indicates the proportion in atomic weights:—

Zinc....................	1·0
Iodine	1·04
Zinc removed by water....	0·45

On distilling off the alcohol in a water-bath, a yellowish liquid remained, which when heated to about 205°, gave off more alcohol,

leaving a dark yellow solid. This when heated over a gas flame, blackened and was resolved into a combustible gas, a small quantity of a liquid having the smell of ether, and a residue from which alcohol extracted zinc iodide, leaving zinc oxide and some carbon.

The original substance is probably an iodo-ethylate of zinc. The original reaction would appear therefore to have been—

$$C_2H_5I + C_2H_6O + Zn = C_2H_6 + \left.\begin{matrix} C_2H_5O \\ I \end{matrix}\right\} Zn,$$

which is perfectly analogous to what has before been supposed to take place in the reaction with water.

$$C_2H_5I + H_2O + Zn = C_2H_6 + \left.\begin{matrix} HO \\ I \end{matrix}\right\} Zn.$$

From this paper it will be gathered that the copper-zinc couple supplies the means of preparing both zinc-ethyl and ethyl hydride on a large scale with perfect ease. Of course the zinc foil may be replaced by granulated zinc. The rapidity and simplicity of the action renders it well suited for lecture illustration.

In another paper we hope very shortly to describe its action on the homologues of ethyl iodide.

XVIII.—*Observations on the Nature of the Black Deposit in the Copper-zinc Couple.*

By J. H. Gladstone, Ph.D., F.R.S., and Alfred Tribe, F.C.S.

A question has been raised as to the nature of the black deposit in the copper-zinc couple that we have lately employed for effecting chemical decompositions, and it has been suggested by Dr. Russell that it contains more or less metallic zinc.

In the present note we give our own observations on the matter; and we are the more glad to do so, as they have a direct bearing on an important point in the history of galvanism.

When a solution of copper sulphate is poured upon zinc, the furry deposit consists of pure copper as long as the solution in contact with the zinc still contains that metal; when, however, the original sulphate has been completely converted into zinc sulphate, other reactions supervene. Through the agency of the oxygen dissolved in the water, a deposit of zinc oxide begins to take place on the copper crystals in the manner described by us in a communication to the Royal Society (*Proc. Roy. Soc.*, 1872, No. 134). The following is the mode of action in

the form of an equation, it being understood that the two metals are in contact :—

$$m\mathrm{Cu} + \mathrm{O} + \mathrm{ZnSO_4} + n\mathrm{Zn} = m\mathrm{Cu} + \mathrm{ZnO} + \mathrm{ZnSO_4} + (n-1)\mathrm{Zn}.$$

At the same time the decomposition of water, which commences as soon as any copper is deposited on the zinc, goes on continuously with evolution of hydrogen, among the copper crystals. But, in addition to this, there is a formation of metallic zinc, which, if the different substances be allowed to remain in contact, becomes considerable in amount.

A quantitative experiment was made by allowing a couple to remain for rather more than two days in contact with a 1·5 per cent. solution of zinc sulphate, shaking off the black deposit, and treating it with dilute acid. The hydrogen evolved amounted to 5·6 c.c. (corrected), which is equivalent to 0·01625 grm. of zinc, while the copper was estimated at 0·218 grm., showing that the deposit contained 7·4 parts of metallic zinc to 100 parts of copper.

That this metallic zinc is not due to the reduction of the oxide produced in the manner mentioned above, was proved by its forming equally well in a solution from which the air had been previously expelled by boiling, and to which the atmosphere had no access during the experiment. Such a deposit appears black, or nearly so, to the naked eye; but when examined by the microscope it is seen to consist of branches of crystallised copper, studded with small crystals of metallic zinc. This metallic zinc is, of course, dissolved at once by dilute acids, with evolution of hydrogen, and uncovering of the copper branches; or if it be washed with a solution of cupric sulphate, the zinc is replaced by the more negative metal.

It would appear, therefore, that in the manner in which we have usually prepared our copper-zinc couple, the deposit can contain little or no metallic zinc. If, however, it be allowed to stand some time before it is washed, it will contain zinc, and as this, in the first instance, actually increases the number of points of contact, it may rather increase than diminish the efficiency of the couple.

In the reduction of silver chloride by zinc, we meet with the same phenomena. As long as there is undecomposed silver chloride, the zinc continues to unite simply with the chlorine; but when there is nothing but metallic silver and zinc in contact and surrounded by zinc chloride and water, zinc begins to be deposited on the surface of the silver.

If an aqueous solution of platinic chloride be poured on to zinc, a portion of it is reduced to platinous chloride, as evidenced by the change of colour, while some is reduced at once to the metallic state, forming a grey coating from which bubbles of hydrogen arise, no doubt from the decomposition of water by the conjoined metals. The

platinous chloride in solution is reduced in its turn, and the black deposit, after standing awhile in the solution of zinc chloride, was found to effervesce on treatment with acid. In two early experiments made in 1871, before we understood the nature of the action, we found respectively 3·0 and 10·7 per cent. of zinc in the two specimens of the deposit.

Terchloride of gold acts in a similar manner. The deposited gold which had stood in the solution of the transformed chloride was found to contain both zinc oxide and metallic zinc.

The platinum-zinc and the gold-zinc couples decompose water much more rapidly than the copper-zinc couple does, as might be expected from the superior position of the negative metals in the electro-chemical series.

In the early days of the galvanic battery, it was observed that when the sulphuric acid had dissolved a good deal of zinc, a deposit of that metal sometimes occurred upon the copper plates, and it was partly on that very account that Daniell proposed his battery in which sulphate of copper is placed in contact with the copper, and sulphuric acid with the zinc. The reaction by which this deterioration of the power occurs in the old forms of galvanic battery may be thus expressed:—

Before contact—

$$m\mathrm{Cu} \mid \mathrm{ZnSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{H_2SO_4} \mid n\mathrm{Zn};$$

After contact—

$$m\mathrm{Cu} \mid \mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{H_2SO_4} \mid \mathrm{ZnSO_4} \mid (n-1)\mathrm{Zn}.$$

Now the simple action of the myriads of circuits in our couple is this—

$$m\mathrm{Cu} \mid \mathrm{H_2O} \mid n\mathrm{Zn},$$

which becomes—

$$m\mathrm{Cu} \mid \mathrm{H_2} \mathrel{\vdots} \mathrm{ZnO} \mid (n-1)\mathrm{Zn};$$

But where the water contains sulphate of zinc, something like the following arrangement of molecules must often occur:—

$$m\mathrm{Cu} \mid \mathrm{ZnSO_4} \mid \mathrm{ZnSO_4} \mid \mathrm{H_2O} \mid \mathrm{H_2O} \mid n\mathrm{Zn};$$

and this will become—

$$m\mathrm{Cu} \mid \mathrm{Zn} \mid \mathrm{ZnSO_4} \mid \mathrm{H_2SO_4} \mid \mathrm{H_2O} \mid \mathrm{ZnO} \mid (n-1)\mathrm{Zn};$$

And this is not the end of the deposition of zinc, for the sulphuric acid thus generated will certainly be swept away by the currents that are produced at the same time, and may in other places set up the same reaction that occurs in the old batteries.

The decomposition of the metallic salt in such an arrangement as Daniell's battery, has sometimes been viewed as the effect of the nascent hydrogen evolved against the copper or platinum plate. The same explanation may be given in this case also, if any prefer it, the nascent hydrogen being derived, not from an acid but from water.

Whichever be the explanation, it is evident that we have here a continuous process, by which, eventually, the whole of the zinc will be oxidised at the expense of the water, but during the process it may not only crystallise on the copper branches, but be repeatedly removed from one place to another.

Whether this deposition of zinc has taken place or not before the couple is washed, matters little to the theory of its action, for wherever the dissimilar metals meet there is produced an effective circuit.

In order to determine whether it is perfectly effective when there is the least transference of zinc, we prepared a couple in the usual way, except that the sulphate of copper was removed before its blue colour was destroyed, and with this couple we completely converted 5 c.c. of ethyl iodide into ethiodide of zinc in twenty minutes, a period shorter than that of the majority of our former experiments.

P.S.—March 20. As the idea seems to be still entertained by some chemists that the deposit owes its black colour in some way to the presence of zinc, it may not be amiss to state more explicitly our view of the matter.

We fully admit that the black deposit in our couple may usually contain small quantities of metallic zinc: for the sulphate of zinc first formed must be often held within the meshes of the arborescent copper to the exclusion of the copper solution, and thus the secondary action will commence in one place before the primary action is completed in another. But we cannot assent to the view that the blackness indicates necessarily the presence of zinc: for, among other reasons,—

The first deposit of copper from a very acid solution of sulphate of copper is black.

Some specimens of the black deposit in our couple give much, some a little, and others no perceptible evolution of gas when treated with hydrochloric acid.

Black deposit containing metallic zinc remains black when treated with sulphate of copper. The copper salt has, of course, destroyed the zinc, as indeed is shown by the deposit no longer effervescing with acid.

Our conviction is that the colour depends mainly on the rapidity of growth of the metallic crystals, and that an arborescent deposit, whether of copper or zinc, if slowly formed, will be black, just as finely divided platinum or gold or silver is black.

XIX.—*On the Formation of Sodium Sulphide by the Action of Hydrogen Sulphide upon Sodium Chloride at High Temperatures.*

By CHAS. T. KINGZETT.

WHILE making some experiments, about a year ago, on the action of coal-gas upon pure sodium chloride at a bright red heat, I found, somewhat to my surprise, that sodium sulphide was formed in small yet decided amount.

Three grams of pure sodium chloride were placed in a combustion-tube and heated sufficiently to fuse the salt, a current of ordinary coal-gas (as manufactured by the gas company of St. Helen's, Lancashire), being meanwhile passed through the tube for an hour. Of the sodium chloride used, 1·74 per cent. was converted into sodium sulphide.

A repetition of the experiment, with approximately the same result, induced me to substitute pure hydrogen sulphide for coal-gas.

The results obtained in several experiments, lasting from ten minutes to three hours, and at various temperatures, are given in the following table:—

Sodium chloride used in experiment.	Duration of experiment.	Temperature employed.	Percentage of sodium chloride decomposed.
3·123 grams.	1 hour.	Sufficient to fuse salt.	6·00 per cent.
3·123 "	"	"	15·00 "
3·123 "	2 hours.	Much higher.	3·38 "
·301 "	10 minutes.	Below fusion.	1·10 "
·7215 "	30 minutes.	"	·94 "
3·0587 "	40 minutes.	Very high.	5·51 "
1·0565 "	45 minutes.	Below fusion.	1·71 "
·844 "	2 hours.	Partial fusion.	2·21 "
2·005 "	1 hour.	To fusion.	·93 "
1·4864 "	"	"	1·78 "
·939 "	2 hours.	"	8·18 "
1·056 "	3 hours.	"	5·99 "
·500 "	2 hours.	"	8·12 "

The sodium chloride decomposed was calculated from the amount of sodium sulphide formed. This was estimated by dissolving the product of each experiment in water, boiling to expel hydrogen sulphide, and then titrating the solution on cooling with decinormal iodine-solution, after the addition of starch-solution and acetic acid; at other times, the boiled solution was titrated with a normal standard solution of sulphuric acid.

The fused mass left as the product in the combustion-tube was always

of a reddish yellow colour, and dissolved in water to a clear, slightly yellow coloured solution.

As might be predicted, and as a glance at the above tabulated experiments confirms, the amount of sodium sulphide formed, other conditions being the same, is found to depend on (1) the temperature employed, and (2) the rate of the current of hydrogen sulphide.

The temperature found most conducive to the formation of sodium sulphide is one sufficient to thoroughly fuse the sodium chloride. The current of hydrogen sulphide must be rapid enough to carry off the hydrogen chloride which is formed, as otherwise it reacts upon the sodium sulphide to reproduce the original substances.

In these experiments the temperature employed in each case was not the same, nor were precautions taken to ensure the same rate of hydrogen sulphide current: hence the apparently anomalous results obtained.

The hydrogen sulphide used was sometimes obtained by the reaction that occurs between sulphuric acid and ferrous sulphide; at others, by the action of hydrogen chloride upon antimonious sulphide, while at times it was obtained by the passage of pure hydrogen over fused sulphur. The last-named method was effected by placing the sulphur in the tube containing the sodium chloride but two or three inches before it. That part of the tube containing the sodium chloride was heated to redness or otherwise as desired, while the flame of a spirit lamp was used to heat that part which contained the sulphur. It is not necessary to dry the hydrogen sulphide used, although if it be not dried, the amount of sodium sulphide formed is slightly increased, because the steam present converts sodium chloride into sodium hydrate and hydrogen sulphide converts this into sodium sulphide.

As at high temperatures hydrogen sulphide is partially decomposed into free hydrogen and sulphur, I considered it desirable to make further experiments. I transmitted pure hydrogen over sodium chloride at a bright red heat, but I never, during my experiments, observed any decomposition; no alkali was obtained. The same remark applies also when sulphur and sodic chloride (both dry) are mixed together and heated to redness. Thus it would appear that the production of sodium sulphide by the action of hydrogen sulphide upon sodium chloride is the result of a direct reaction viz. :—

$$2NaCl + H_2S = Na_2S + 2HCl.$$

But more experiments are being made to show whether this is the only reaction that occurs in the tube at present. I am inclined, from an examination of the gaseous products, to think that other reactions take place.

XX.—*An Air-bath of Constant Temperature between* 100° *and* 200° C.

By Hermann Sprengel.

The temperature of boiling water, varying but slightly with the atmospheric pressure, is (on account of its easy attainment) the acknowledged standard in operations, such as drying. But if the degree of temperature has to be higher or lower than this, we generally avail ourselves of gas-lamps, whose heating power is regulated by an automatical action, existing between the heated medium and the supply of gas which feeds the lamp. as in Scheibler's ingenious electro-magnetic apparatus (*Zeitschrift für analytishe Chemie*, vol. vii, p. 88, 1868). Simplicity, however, speaks in favour of the water-bath principle (Tichborne's and E. Reynolds' glycerin-bath, *Chem. News*, vol. iv, p. 319, 1861; Deville and Troost's boiling zinc, cadmium, sulphur, mercury, *Compt. rend.*, lvii, p. 897, 1863), and I must plead this as an excuse for describing an arrangement which may be considered obvious.

My instrument (almost a copy of the common water-bath) is charged (in place of water) with a liquid boiling without decomposition at the desired temperature, and is made of a material on which this liquid, even whilst boiling, does not act, or at least not readily. Such is the case with diluted sulphuric acid and lead, if the temperature required is not much above 150°.

The top of the leaden air-bath is provided with an upright worm, cooled by air, in which the vapour from the boiling acid condenses. The products of condensation, thus continually flowing back to the acid, cause the latter to remain unaltered both in volume and in specific gravity. and therefore in its boiling point.

The outside case of the double-walled air-bath is a $6\frac{1}{2}''$ cube; the inside a 5″ cube. The worm, made of about 30′ of gas-piping of $\frac{3}{8}''$ diameter, is 15″ high and 4″ wide. The coils of the worm are kept apart from each other $\frac{1}{8}''$ by means of solder; and the worm is kept in its upright position by two iron supports, soldered to the sides of the air-bath. The top is likewise provided with a stoppered neck, through which the outer chamber may be filled with the acid, and with an aperture leading to the inner chamber for the purpose of holding a thermometer. The door is a sliding one, and made of copper or glass. The lead is about $\frac{1}{10}''$ thick, and weighs 6 lbs. to the square foot. The weight of such an apparatus is 30 lbs., and its cost (labour excluded) about 15*s*. All joints coming in contact with the acid,

should be of lead, *i.e.*, should be fused together by means of the hydrogen blowpipe.

For fear of destroying the lead too quickly, it is not advisable to use the acid stronger than 1·74 sp. gr., boiling at 200° C. (*vide* Dalton's tables). My personal experience lies within the limits of a few trials, made with an acid of 1·55 sp. gr., boiling at 150°. Four years ago, however, I had such an air-bath made for Dr. Völcker, who has been using it ever since for maintaining a constant temperature of 150°. On his authority I am permitted to state, "that the apparatus has given every satisfaction, and that the bottom only required renewing after an almost daily use of three years."

If the acid has once been brought to the desired boiling-point, the management of the apparatus demands no further care than to light a gas-lamp of such a power underneath it, that the steam of the boiling acid rises to about the middle of the worm. This limit, recognisable by touch, will eventually rise or fall in harmony with a more or less rapid ebullition produced by any accidental increase or decrease of the flame. It is better to have the worm removed from the heated atmosphere over the air-bath to a cooler one, or replaced (for the same reason) by a long condensing tube of lead or glass, either upright or slanting. This tube need not be a fixture, but may be fitted into a projecting and conical neck in the top of the air-bath. For obvious reasons such a tube may be recommended as a convenient appendage to the ordinary water-bath.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Refraction-equivalents of the Elements Carbon, Hydrogen, and Oxygen. By R. LANDOLT (Chem. Centr., 1872, 705).

THE values obtained for these elements, from an examination of compounds belonging to the fatty series, is found to be too small when applied to the aromatic series. A constant refraction-equivalent, however, is found for the C_6 nucleus in the various benzene derivatives when the refraction-equivalents taken for the carbon, hydrogen, and oxygen of the side-chains are those of the above-mentioned elements in the fatty series.

C. E. G.

Modular Properties of Refractive Powers in Saline Solutions. By C. A. VALSON (Compt. rend., lxxvi, 224—226).

AFTER referring to the calorific modulus of radicals whose existence has been proved by Favre and Silbermann, and those of capillarity and density, an account of which he has already published, the author deduces from the experimental results of M. Fouqué (*Ann. de l'Observatoire*, ix), that the variations in the refractive power of a solution are sensibly proportional to the amount of salt dissolved, and that, in passing from one salt to another, the metallic radical remaining the same, the refractive power varies by a quantity which is sensibly constant, and which he calls the *modulus of the refractive power*. The same happens when the metalloïdal radical varies, so that "in passing from one saline solution to another, each of the two saline radicals causes the refractive power to vary by the same quantity, whatever the other radical may be with which it is associated."

The following is a list of the values of the modulus in thousandths (·001), which must be added to or subtracted from 0·757, the refractive power of a normal solution of potassium sulphate to obtain the refractive power of any other normal saline solution.

Metallic Radicals.—K = 0, Na = 4, NH_4 = 20, Li = 14, Ca = 9, Mg = 10, Al = 11, Ba = − 17, Mn = 3, Zn = 0, Cu = 1, Cd = −13, Pb = −27, Th = −67.

Metalloïdal Radicals.—Sulphates zero, nitrates 3, chlorides 15, bromides zero, iodides—5, carbonates 8, bicarbonates 11, chromates 19, bichromates 15.

It will be remarked that the refractive power is greater for the alkali-metals, and especially for those whose atomic weights are the smallest. These relations have a special interest considered from a mechanical point of view: for the refractive power $\frac{n^2-1}{\rho}$ measures the loss of *vis*

viva produced in the light which traverses the medium, so that "in normal saline solutions, each of the elementary radicals of the salt exercises an action upon the light peculiar to itself, and independent of the other radicals with which it may be associated."

C. E. G.

Spectrum of the Bessemer Flame. By W. MARSHALL WATTS (Phil. Mag. [4], xlv, 81—89).

THE author shows, by a comparison of the Bessemer, Manganese oxide, and Spiegeleisen spectra, that the greater number of the lines in the former spectrum, being those which disappear at the moment when the "blow" is finished, are due to manganese oxide. The kind of iron used influences the brightness of several groups of lines to a considerable extent.

By holding wires of gold and platinum in the flame, it was noticed that at the beginning of the "blow" the temperature is below that at which gold melts (1300° C.), that it gradually rises to and exceeds this temperature, but never reaches that of molten platinum (2000°).

M. M. P. M.

New Method of Exhibiting the Spectra of Metals. By TH. EDELMANN (Chem. Centr., 1872, 691).

A SALT of the metal whose spectrum is required, together with some picrate of ammonium, is made into a paste with a little alcohol, and introduced into a hollow cylinder, made of Bunsen's carbon. An oxy-hydrogen flame made to issue from this cylinder, is intensely coloured, and was found to give a very fine spectrum of any of the following metals:—Na, Tl, Sr, Ba, Ca, Cu, Bi.

R. S.

On the Influence of Inactive Solvents on the Specific Rotatory Power of Active Substances. By A. C. OUDEMANS, Jun. (Ann. Chem. Pharm., clxvi, 65—77).

IN the determination of specific rotatory power, it has been usual hitherto to proceed upon the tacit assumption that the nature of the solvent is immaterial, provided it is itself optically inactive and exerts no chemical action on the substance dissolved. It was, however, pointed out by Biot (*Mém. de l'Académie*, xv, 93), that this was not the case, and attention has been drawn to the same fact more recently by Jodin (*Compt. rend.*, lviii, 613).

The author has determined the specific rotatory power of a number of substances of different chemical character, including cane sugar, cubeb oil, several alkaloïds and their salts, and other bodies. He has found that when different menstrua are employed for dissolving the same substance, different values are generally obtained, even at the same temperatures and the same degree of concentration.

Thus, when cane sugar is dissolved in water, its specific rotatory power is 66·9°, in alcohol of 50 p. c., it is 66·4°. This difference is very small,

but the author believes that it cannot be attributed to experimental error. In other cases, much greater differences are observed, as for instance, in the case of brucine, the specific rotatory power of which, when dissolved in alcohol, is −85°, but in chloroform −119° to −127°.

The author has likewise observed that when an active substance is dissolved in a mixture of two solvents, its specific rotatory power assumes a new value, which has no evident relation to the values obtained when the two solvents are employed separately. For example in the case of cinchonine, its specific rotatory power in pure alcohol is 228°, and in chloroform 212°; but in mixtures of these two liquids the value varies considerably, rising to the maximum in a solution prepared with a mixture of 10 p. c. alcohol and 90 p. c. chloroform, when it approaches 240°.

In an alcoholic solution of cinchonine, about half the alcohol may be replaced by chloroform without any marked effect on the specific rotatory power. On the other hand, if in a chloroform solution even $\frac{1}{300}$ of the chloroform be replaced by alcohol, a difference of 4° is at once produced. Hence it appears that from the influence of any two inactive solvents separately on the specific rotatory power of an active body, no conclusion can be drawn as to the influence of a mixture of the two. Consequently, in experiments of this kind, it is advisable to make use of solvents in as pure a state as possible, and especially in the case of alcohol is it necessary to employ either absolute alcohol or spirit of constant strength, since mixtures of alcohol and water may be expected to exercise the same kind of influence that has been observed in the case of alcohol and chloroform.

Biot endeavoured to explain the influence of concentration on the specific rotatory power by supposing the formation of molecular combinations between the active substance and the solvent. The author thinks it not improbable that such molecular combination may be the explanation of the changes observed by him. He has, accordingly, made some experiments in order to test this view. He finds that, generally speaking, the specific rotatory power of a substance is highest when the menstruum employed is that liquid in which it is most soluble.

In the case of cinchonine which has been already quoted, there is an evident connection between the increase in the specific rotatory power of the alkaloïd when dissolved in a mixture of alcohol and chloroform, and the increase of solubility in the mixture.

The solubility of cinchonine in such a mixture has been determined, and it turns out that, although cinchonine is less soluble in chloroform than in alcohol, there are certain mixtures of the two in which it is more soluble than in either alone, the maximum of solubility being reached when twenty parts of alcohol are mixed with eighty parts of chloroform.

The author believes his hypothesis to be in the main confirmed, but has not overlooked the fact that the *maximum* of the specific rotatory power does not coincide with that of solubility; neither does the increase in the former proceed *pari passu* with the increase in the latter on the addition of chloroform to an alcoholic solution of the alkaloid.

In a postscript the author draws attention to some experiments of

Dr. J. L. Hoorweg (*Maandblad voor Natuurwetenschappen* [3], i, 12), on strychnine and acetate of morphine which entirely confirm his own results.

W. A. T.

Colouring of Glass by Insolation. By J. Henrivaux (Bull. Soc. Chim. [2], xix, 54).

The colour developed in certain kinds of glass containing manganese upon exposure to sunlight, is regarded by the author as due to oxidation.

W. A. T.

Galvanic Polarisation of Platinum. By H. Helmholtz (Chem. Centr., 1872, 689).

It follows from Faraday's electrolytical laws that decomposition of water by the galvanic current is possible only when the chemical processes in the battery taken together can produce more heat than the oxygen and hydrogen generated in the voltameter, and therefore that about $1\frac{3}{4}$ Daniell's cells are required for a continuous decomposition of water. A single Daniell's cell in connection with platinum electrodes in dilute sulphuric acid is not capable of producing visible decomposition; it only causes polarisation of the electrodes, that is to say, a new arrangement of the atoms of the liquid by which potential energy is accumulated, so that the voltameter may be looked upon as a condenser of immense capacity. It might be expected that the quantity of electricity thus lost in the voltameter could be recovered in the current which arises on connecting the platinum electrodes with each other. But experiment proves that this is not the case.

As the author had before observed that the atmospherical oxygen dissolved in the water took part in the electrolytic decomposition, the voltameter was connected with a mercury pump, and the water was, by long continued pumping, completely freed from all dissolved gases. But even then the polarising and the depolarising currents were not fully equivalent to each other. This remarkable fact may perhaps be explained by assuming for water, as Faraday has done, a certain non-electrolytical conductivity such as is possessed by ice.

The author, however, who had found that platinum electrodes saturated with hydrogen allow the current to pass through the liquid for many hours without polarisation and without any diminution of its strength, proposes another explanation for the transmission of electricity through water without visible electrolytical decomposition. He assumes that the oxygen, which under the influence of the current is directed towards one electrode, combines with the previously free hydrogen, whilst the hydrogen at the other end of the polarised row of water-molecules becomes free to diffuse itself through the water. The electrolytical decomposition would thus be, as it were, undone, the whole result of the action of the current being a different distribution of the free hydrogen. Oxygen dissolved in the water, or condensed on the platinum plates, acts in a similar manner, though of

course in opposite direction; its action is not so marked as that of hydrogen,—probably on account of its inferior power of penetrating into the platinum.

As the liberated hydrogen diffuses itself through the water and may even pass on to the other platinum plate and renew its charge, it is evident that the current may continue for an indefinite time.

When the hydrogen is set free very rapidly, part of it assumes the gaseous state instead of being absorbed; this agrees with an observation made long ago by Poggendorff, that a single Daniell's cell is capable of producing evolution of hydrogen when platinum electrodes charged with hydrogen are used.

In all those cases where the gases dissolved in the liquid electrolyte play an important part, the strength of the current can be increased by stirring or shaking the liquid. As long as the platinum plates retain any hydrogen, the current is not stopped by depriving the liquid of all dissolved gas; but it gradually becomes very feeble. The current obtained by connecting two polarised electrodes is at first strong, but sinks rapidly, and after some time continues without any further diminution of its strength; indeed the author has found that the strength of all currents maintained either by hydrogen which gradually makes its way from the interior to the surface of the platinum plate, or by gases dissolved in the liquid electrolyte, is quite independent of the resistance of the circuit. Even several hundred miles of telegraph wire, on being inserted in the circuit, caused only a momentary change in the intensity of the current.

The saturation of the platinum plates with hydrogen was accomplished by closing the liquid from below with mercury containing zinc, and maintaining for days a feeble evolution of hydrogen from both plates, whilst the electrolytically liberated oxygen combined with the zinc.

R. S.

Action of a Copper-Cadmium Couple on a Solution of Cadmium Sulphate. By F. RAOULT (Compt. rend., lxxv, 1103).

Two plates, one of copper and one of cadmium, are completely immersed in a solution of cadmium sulphate deprived of air and covered with a layer of oil. As long as the two plates do not touch, a very slight disengagement of hydrogen is observed on the cadmium plate, which is feebly attacked, whilst the copper undergoes no visible change whatever. As soon, however, as by a suitable movement of the vessel the plates are made to touch, cadmium begins to be deposited on the copper plate, giving to the latter the appearance of cadmium.

R. S.

Apparent Replacement of Certain Metals by themselves in their Solutions. By F. M. RAOULT (Compt. rend., lxxvi, 156).

A *gold-cadmium* couple immersed in a concentrated and boiling solution of cadmium sulphate or chloride, decomposes these salts, and in less than a minute a white, brilliant, and firmly adherent film of cadmium is precipitated upon the gold. No advantage is gained by acidulating

the solution, the action being rapid even when the salt is perfectly neutral, and when not a trace of hydrogen is disengaged. The experiment does not succeed with the nitrate.

A *gold-zinc* couple decomposes in a similar manner concentrated solutions of the sulphate or the chloride of zinc (not the nitrate), the gold immediately becoming covered with a white film of zinc.

A *gold-tin* couple decomposes a concentrated and boiling solution of stannous chloride, a film of tin being formed on the gold.

The gold of these couples may be replaced by copper; in all cases the quantity of metal precipitated is insignificant.

The couples gold-iron, gold-nickel, gold-antimony, gold-lead, gold-copper, gold-silver, on being immersed in cold or boiling acid or neutral solutions of the metal which is in contact with the gold, do not precipitate the dissolved metal upon the gold, even under the influence of a current of hydrogen.

The deposits cannot be removed except by the prolonged action of boiling acids, and, as on all those parts where there had been a precipitate of metal, the plate of gold had lost its lustre, its colour being turned to orange-brown, it appears that the gold had undergone a certain disaggregation such as would be brought about by the superficial formation of an alloy.

R. S.

A New Form of Nöe's Thermo-electric Battery. By A. v. WALTENHOFEN (Chem. Centr., 1872, 530; see also this Journal, 1871, p. 989).

THE negative wire which is fused to the positive metal, is bent back from the point of contact at an acute angle. A small metallic rod is fused to the two elements at this same point. Twenty elements are arranged in a circle, the metallic rods just mentioned being in the centre. The space in the centre is covered with a plate of mica, and the metallic rods are then heated by means of a circular gas flame.

The electromotive power of twenty such elements is equal to 19·4, one Bunsen cell being equal to 20. If a Daniell cell be equal to 12, then one of these cells is about equal to 1. The resistance of each element = ·056.

M. M. P. M.

Determination of Degrees of Temperature in Absolute Units. By L. LORENZ (Pogg. Ann., cxlvii, 429—452).

THE unit of heat, being equivalent to the unit of work, can be expressed in the absolute units of time, mass, and space; but the degrees of temperature hitherto used, are not expressed in absolute measure, as they refer to the specific nature of a particular substance, *i.e.*, water. The author proposes an absolute standard of temperature.

The heat-unit, which is taken = 433 milligram-meters, can be represented by $433 \times 9806 = 425 \times 10^7$, inasmuch as the weight of 1 milligram contains 9806 absolute units of force (the acceleration by gravity expressed in millimeters). The value of the heat-unit in absolute measure will be denoted by A.

Now 2·436 heat-units are required to heat 1 milligram of hydrogen through 1° C, or expressed in absolute units—

$$2{\cdot}436A = 2{\cdot}436 \times 425 \times 10^7 = 1035 \times 10^7$$

when the volume remains constant.

The author now defines as *a degree of temperature in absolute measure, the rise of temperature which is produced by the absolute heat-unit in that number of (gaseous) elementary atoms (under constant volume) which in a normal case of electrolysis is liberated by the current unit of strength in the unit of time.* For instance, in the electrolysis of HCl, there are as many atoms of H and Cl liberated by the unit of electricity, as there are atoms in $\frac{1}{480}$ milligram of hydrogen, and this quantity of hydrogen, in order to be raised 1° C., requires, in absolute units

$$\frac{2{\cdot}436}{480} A = 0{\cdot}005075A = 216 \times 10^5,$$

so that the absolute degree of temperature would be $= \frac{1}{216 \times 10^5}$ degrees centigrade; and on the other hand—

$$1° \text{ C.} = 216 \times 10^5 \text{ in absolute units.}$$

Since, according to the law of Dulong and Petit, the rise of temperature produced by the heat-unit in equivalent numbers of elementary atoms is the same, the degree of temperature, as given above, is evidently independent of the specific nature of any particular substance.

In the remainder of the paper the author arrives, through lengthy mathematical considerations, at the following results—

1. It is probable *that the ratio of the conductivities for heat and electricity in perfectly pure metals is proportional to the temperature, reckoned from its absolute zero.*
2. *This ratio is exactly equal to the temperatures reckoned in the absolute scale and in absolute units.*
3. *The maximum of temperature (expressed in absolute units) which can take place between two points of a conductor is always numerically smaller than half the difference of the electric tensions at these two points.*

R. S.

The Specific Heat and other Physical Characters of Mixtures of Methylic Alcohol and Water, and Certain Relations existing between the Specific Heat of a Mixture, and the Heat Evolved or Absorbed in its Formation. By A. Dupré (Proc. Roy. Soc., xx, 336—342).

The communication is divided into seven sections, each section detailing respectively the method and the results obtained in the examination of one of the physical characters of a mixture of methylic alcohol and water; the alcoholic strength of the mixture increasing or decreasing in regular proportion.

A table accompanies each section, in which the results of experiment are contrasted with those obtained by calculation.

1. Specific heat.
2. Heat produced by mixing methylic alcohol and water (the figures represent the units of heat evolved in the formation of 5 grams of the mixture).
3. Boiling points.
4. Capillary attraction.
5, 6. Specific gravity and rate of expansion.
7. Compressibility.

The results of experiment always deviated from the calculated mean. In some cases the values found were below, in others above the calculated mean; at the same time a numerical relation is observable between two tables, and by employing an arbitrary factor, one table may be readily converted into another. Thus, for example, if the heat evolved in the formation of 5 grams of any of the mixtures be divided by 7·9, the elevation of the specific heat of this particular mixture above its calculated mean value is obtained. A similar relation exists between any two other tables, but the arbitrary number required to convert them varies with the physical character.

The relation existing between the specific heat of mixtures and the heat evolved in their formation, may be expressed by the following laws:—

1. The difference between the number of heat-units evolved during the mixing of given weights of two substances, at the temperatures t and t' respectively, is equal to the difference between the number of heat-units required to raise the mixture, and that required to raise the two constituents taken separately, from the lower to the higher temperature. Or let U and U′ be the units of heat evolved by mixing x and y at the temperatures t and t' respectively; S, S′, and S″ the specific heat of the mixture z and its constituents x and y respectively: then

$$\mathrm{U}-\mathrm{U}' = z\,.\,\mathrm{S}(t-t')-\{x\,.\,\mathrm{S}'(t-t') + y\,\mathrm{S}''\,(t-t')\}.$$

2. If more units of heat are evolved at the higher than at the lower temperature, the specific heat of the resulting mixture will be below the calculated mean, and *vice versâ*.

3. The absorption of a lesser number of heat-units will of course be equivalent to the evolution of a greater number, while the absorption of a greater number will be equivalent to the evolution of a smaller number of heat-units.

The author concludes by showing that a great many mixtures of various liquids, upon which he has specially experimented, conform as closely as can be expected with proposition I, and generally that, if these propositions prove to be an exposition of a general law, it is possible to calculate the specific heat of one constituent of a mixture or solution, if the specific heat of the other constituent, the specific heat of the mixture, and the heat evolved or absorbed at two different temperatures between which these specific heats have been estimated, be known. It will also be possible to compare the specific heat of liquid and solid substances, when both are placed under similar conditions.

J. W.

Condensation of Gases on the Surface of Solid Bodies. By F. Weber (Chem. Centr., 1872, 689).

Glass on the surface of which hydrogen, air, carbonic acid, and sulphurous acid had been condensed at a temperature of 0°, was heated to 100°. The quantities of the different gases thrown off by this rise of temperature were found to be proportional to the square roots of their densities.

R. S.

Transpiration of Gases. By O. E. Meyer and Springmühl (Chem. Centr., 1872, 689).

Poiseuille's law for liquids was proved to hold good for gases. The coefficient expressing the influence of a rise of temperature upon the friction of the gases is about three-quarters of their coefficient of expansion.

R. S.

The Transpiration of Saline Solutions. By F. Schulze (Chem. Centr., 1872, 705—707).

In this paper,—a continuation of one published in Poggendorff's Annalen—an account is given of the method employed by the author for determining the rate of efflux through capillary tubes of solutions of various salts containing one part of salt to ten of water. The apparatus for this purpose consisted of a tube ·4 meter long and ·02 in diameter, drawn out, and having a capillary tube fused into one end. Two rings at a distance of ·3 meter apart were placed on the larger tube, which was filled with the solution, the time being noted when the level of the liquid had reached the upper and lower rings respectively, the difference being the time which had elapsed whilst a given quantity of liquid had flowed through the capillary tube. The experiments were repeated with five different tubes, and as the density of the solutions, the temperature, and the pressure were sensibly equal, the results obtained for each tube are directly comparable. These are tabulated, and it would appear, with respect to the potassium, sodium, and lithium solutions, as also the barium, strontium, calcium, and magnesium solutions, that the velocity is greater the greater the atomic weight of the metal, and that there is but little difference between the velocity of solutions of the chloride, bromide, or iodide of any one metal.

C. E. G.

On the Statics of Saline Solutions. By M. Berthelot (Compt. rend., lxxvi, 94—98).

The general opinion that salts in solution react upon one another in such a manner that the strong acids combine with the strong bases, leaving the weak acids to the weak bases, is confirmed by observations of the thermic effects. The salt, whose formation disengages the most heat, is that which is produced whenever the salts at whose expense it is formed are in a state of partial decomposition in the solution. For

instance, in the case of the mutual decomposition of ammonium sulphate and potassium carbonate, it is known that the ammonium salt is decomposed to a slight extent ($\frac{1}{200}$) when dissolved in water, acquiring an acid reaction; this free acid is neutralised by the potassium carbonate, with simultaneous formation of ammonium carbonate, and a fresh portion of sulphuric acid is set free from the ammonium sulphate, which is again neutralised by the potassium carbonate, and so on until, if there be equivalent quantities of the salts in solution, the whole, or nearly the whole of the potassium salt is converted into sulphate. Similar effects are produced with ferric sulphate or nitrate in presence of sodium acetate, it being known that the ferric salts undergo partial decomposition when in solution, the thermic effects produced proving that these decompositions really take place. It is a general rule that all chemical changes accomplished without the intervention of some external force tend to the production of that body, or system of bodies, which disengages the most heat.

C. E. G.

Supersaturated Saline Solutions. By ARCHIBALD LIVERSIDGE (Proc. Roy. Soc., xx, 497—507).

IN the first instance, the author attacks the theories propounded by Mr. Tomlinson, namely, that crystallisation of supersaturated solutions is due to the presence of greasy or other matters in the form of thin films; that certain liquids, such as absolute alcohol, act as nuclei in determining the solidification of such solutions by separating water from the solution, whereas the thin film, on the contrary, owes its activity to the greater attraction which it has for the salt held in solution.

The experiments appear to have been conducted with great care. The solutions were not, in any instance, after saturation, exposed directly to the air, not even in introducing the substance, by means of which it was proposed, if possible, to determine the crystallisation of the solution. When a liquid nuclear agent was employed, it was enclosed in a small glass bulb with a long neck drawn out to a fine point. The tube was surrounded by cotton-wool, and inserted into the neck of the flask containing the hot supersaturated solution. When the latter had cooled, a drop of the liquid was delivered by warming the glass bulb. With the experiment arranged as above, alcohol and sulphuric acid were found to be perfectly inactive.

Solid dehydrating agents, such as calcium chloride, phosphoric anhydride, and quicklime, were also incapable of starting crystallisation. These latter substances were enclosed in glass bulbs, which having been placed in the hot solution, were broken by means of a glass rod at a subsequent stage of the operation.

By a modification of the foregoing glass bulb, thin films of various oils were formed upon the surface of supersaturated solutions. The film, although often of sufficient tenuity to be iridescent, was incapable of inducing crystallisation; and solutions of sodium sulphate, having thin films of oil, benzene, turpentine or citronella oil, upon their surfaces, were preserved for many months without crystallisation super-

vening; that they had not, during that period, lost sensitiveness was proved by starting the crystallisation in the ordinary manner.

Ethereal solutions of oil were likewise inactive as nuclei.

It is suggested, in explanation of the results obtained by Mr. Tomlinson, that in his experiments, since the flask was opened and exposed to the air, in order to place the agent upon the solution, an opportunity was afforded for active nuclei to gain entrance.

A crystal of normal sodium sulphate, containing ten molecules of water of crystallisation, although chemically clean, and indeed obtained directly from the supersaturated solution itself, always induced instantaneous crystallisation throughout the mass. It was not necessary that the crystal should be placed or dropped into the solution, but the instant that the extreme point of a crystal touched the surface of the liquid, crystallisation immediately started from that point. It was further observed that a crystal of sodium sulphate was perfectly inactive when added to a supersaturated solution of alum, or magnesium sulphate, and that a crystal of either of the latter salts likewise failed to induce crystallisation in a solution of sodium sulphate.

The experiments, and the manner in which the active crystal was obtained, were infinitely varied, but always with the same uniform result.

The author confirms the analyses of Löwel and Faraday respecting the composition of the crystals of sodium sulphate formed by the spontaneous evaporation of a supersaturated solution of the same. The mean result of seven analyses gave 46·84 per cent. of water of crystallisation, the salt having been dried at 100°. The formula, $Na_2SO_4 + 7H_2O$ requires 47·01 per cent.

J. W.

Researches on Supersaturation. By A. MICHAELIS (Chem. Centr., 1872, 705).

WHEN a crystal of solid PCl_3Br (?) is introduced into a mixture of phosphorus chloride and bromine, it solidifies: this effect is not produced by indifferent solid substances, or by phosphorus pentachloride or pentabromide. When cooled to —15°, it likewise solidifies, but the crystals produced melt again as the temperature rises. The author has also found that a portion of the solid, added to melted phosphorus sulphobromide, causes its solidification.

C. E. G.

Saturated and Unsaturated Solutions. By A. HANDL (Chem. Centr., 1872, 531).

THE degree of solubility of a substance in a liquid is not, according to the author, regulated by a specific capacity for solution, but by a constant proportion between the amount of substance which dissolves and that which again crystallises out.

M. M. P. M.

Crystallographic Notes. By V. v. Lang (Chem. Centr., 1872, 535).

The potassium, ammonium, ethylamine, aniline, pyridine, and lutidine salts having the general formula, $RCl + C_2H_4.PtCl_2$, have been examined by the author. The first three are isomorphous, probably also the aniline salt, and belong to the monoclinic system.

The pyridine salt crystallises in rhombs, while the lutidine salt belongs to the triclinic system.

M. M. P. M.

Simple Arrangement for the Employment of Gas as a Means of obtaining High Temperatures. By L. Forquignon and A. Leclerc (Compt. rend. lxxvi, 116—118).

The authors have arranged a small furnace, for use with the ordinary gas blowpipe, by means of which platinum and porcelain crucibles of 15 to 20 c.c. capacity may be quickly raised to a temperature considerably exceeding the melting point of cast-iron.

The furnace in question is composed of two parts, an interior envelope and a movable covering. The latter, which completely surrounds the internal portion, rests upon a flange adapted to the outside and lower extremity of the interior envelope. Its walls are very thick, the better to retain the heat, and upon its lower edge eight holes are symmetrically placed, in order to allow an outward passage for the heated gases. A knob or ring of iron at the top serves to remove and to replace this covering. The crucible to be heated is held in the centre of the interior portion by a platinum support, which rests upon a small ledge. The source of heat—an ordinary gas blowpipe, as before mentioned—is arranged beneath in such a manner that the nozzle of the blowpipe shall be only a few centimeters below the inferior circular orifice; the flame will therefore circulate in the first instance round the crucible, then in the annular space comprised between the interior envelope and the covering, and the products of combustion will finally escape by passing out through the eight openings at the base of the latter. The progress of the heating may be observed by holding a small mirror beneath the arrangement.

With a furnace arranged in the manner above described, the authors have succeeded in melting 40 grams of cast-iron in less than a quarter of an hour.

J. W.

Temperature-Regulator for Gas and Lamp Flames. By J. Martenston (Chem. Centr. 1872, 513—514).

A narrow glass cylinder filled with air is placed in the air-bath, the outer part being narrowed to the diameter of a tube which is connected with a U-tube, the bend of which is filled with mercury. Through a cork in the other limb of the U-tube passes a tube which leads the gas to the Bunsen lamp used for heating the bath; this tube is somewhat narrowed at that end which passes into the U-tube, and it is so arranged that it may be made to dip into the mercury if required. A

second tube also passes into the U-tube (for leading in the gas), having a side tube branching off from it connected by caoutchouc with a small tube at which the gas may be burned, the orifice of this latter being situated at about 2 cm. from the top of the Bunsen burner. The tube connecting the glass cylinder (which serves as an air thermometer) with the U-tube, has a small side opening, which may be closed by means of a little caoutchouc cork. The gas-delivery tube is withdrawn from the mercury, the gas turned on, and both flames lighted. When the temperature is within a few degrees of that required, the small opening in the tube leading from the cylinder is closed. When the temperature has been raised to one degree below the desired point, the supply of gas to the Bunsen is shut off by bringing the end of the tube a very little way under the mercury in the bend of the U-tube. The small flame at the orifice of the side-tube then increases, while the Bunsen burner is extinguished. Whenever the temperature sinks slightly the end of the gas tube again appears above the mercury, and the gas is again supplied to the Bunsen, which is lighted by the small flame.

A temperature varying only $\pm$ ·25 may thus be maintained for many hours. The author also describes an arrangement by which—making use of an electric battery—the regulator may be applied to the flame of a spirit lamp.

M. M. P. M.

Water-bath with Self-acting Draught. By M. BURSTYN (Zeitschr. Anal. Chem., xi, 175).

IN this apparatus the steam of the bath can only escape through a tube drawn out at its extremity; this is enclosed in another tube, which falls 2—3 mm. short of its extremity, and is connected by a side-tube with a funnel which completely covers the evaporating basin. In this way a draught of air over the surface of the liquid is produced equal to 9—10 cm. water-pressure.

E. D.

On the Causes of Crystallisation in Supersaturated Solutions. By L. C. DE COPPET (Compt. rend., lxxvi, 434—436).

On a Voltaic Standard of Electromotive Force. By LATIMER CLARK (Proc. Roy. Soc., xx, 444).

Inorganic Chemistry.

The Absorption of Ozone by Water. By L. CARUS (Phil. Mag., [4], xliv, 544).

THE author's researches confirm the statement of Soret, that water absorbs ozone.

He passed ozone, produced by electrolysis of sulphuric acid spread out and kept at 0° C., for two or three hours through water kept at

from 2° to 4°, and found in three experiments that the water contained per litre 5·11 c.c., 4.24 c.c., and 3·86 c.c. of ozone.

The water was proved to be free from oxygenated water and nitrous acid.

Analyses of the ozonized water of Krebs, Kroll, and Co. gave 4·06 to 4·45 c.c. of ozone per litre. The absence of oxygenated water, and of nitrous and nitric acids was proved in this case also.

The ozone was estimated by the decomposition of potassium iodide.

G. T. A.

On Some Properties of Anhydrous Liquefied Ammonia. By G. Gore (Proc. Roy. Soc., xx, 441).

This investigation was made for the purpose of ascertaining the general solvent properties of the liquid, and to detect any manifest chemical reactions between it and various substances. The method employed was precisely similar to that used in the examination of liquid cyanogen (see *Proc. Roy. Soc.*, No. 131, 1871), the tubes being charged with anhydrous chloride of calcium previously saturated with the ammonia vapour.

Two hundred and fifty substances were submitted to contact with the liquid, and the general results in each case were recorded. The only elementary substances soluble in it were the alkali-metals proper, also iodine (bromine was not tried), sulphur, and phosphorus. The more frequently soluble inorganic salts were nitrates, chlorides, bromides, and iodides; whilst oxides, fluorides, carbonates, sulphides, and sulphates were very generally insoluble. Many saline substances, especially certain chlorides, bromides, iodides, and sulphates, absorbed ammonia freely, and swelled greatly, but did not dissolve. The behaviour of the chlorides of mercury was peculiar.

Various compounds of carbon were submitted to the action of the solution of potassium in the liquefied vapour; the free potassium disappeared, but no elementary carbon was liberated.

Solubility of Silica in Aqueous Ammonia. By A. Souchay (Zeitschr. Anal. Chem., xi, 182).

The author has tested the accuracy of the statement of R. Pribram (*Vierteljahresschr. pr. Pharm.*, xvi, 30; *Zeitschr. Anal. Chem.*, vi, 119), that silica in all its forms is more or less soluble in aqueous ammonia, and finds himself able to fully confirm it.

E. D.

Behaviour of Certain Metals with a Solution of Potassium Ferricyanide. By R. Böttger (Chem. Centr., 1872, 708).

Graham has remarked, as a peculiarity of palladium saturated with hydrogen, that it reduces potassium ferricyanide to ferrocyanide; the author finds however that palladium itself possesses the same property. If pure palladium foil be immersed in a dilute solution of potassium

ferricyanide for ten minutes, the latter will bef ound to yield a precipitate with a ferric salt, showing the presence of ferrocyanide. Thallium, magnesium, and arsenic possess a similar reducing power, whilst platinum, zinc, cadmium, aluminium, copper, indium, lead, cobalt, silver, mercury, tin, bismuth, antimony, gold, tellurium, manganese, and iron, have no action.

When a thin sheet of any metal, with the exception of platinum or gold, is immersed in a dilute solution of potassium ferricyanide mixed with ferric chloride, it becomes coated in a short time with a thin, adherent film of Prussian blue. Platinum and gold in contact with an electronegative element, such as antimony or gas-carbon, likewise become covered with a blue film, and as the noble metals, in this instance, are electropositive, the experiment differs from that of Schönbein, who observed that platinum, when made the negative electrode, becomes coated with Prussian blue.

C. E. G.

Preparation of Potassium and Sodium Hydrate.

By E. Pollacci (Gazzetta Chimica Italiana, ii, 379—380).

The author finds that the potassium hydrate prepared by Wöhler's method of fusing nitre with metallic copper and treating the product with water, invariably contains copper oxide, but on substituting iron for copper, a pure product is obtained readily and economically. When nitre is mixed with two or three parts of iron filings, and exposed to the action of heat in an iron vessel, the action spreads rapidly, and the whole mass becomes incandescent. As soon as it is cool, the product is treated with water, and the clear solution decanted and evaporated in the usual manner. The process answers equally well for the preparation of pure sodium hydrate from sodium nitrate.

C. E. G.

Preparation of Rubidium from Beet-root Ash.

By C. Pfeiffer (Dingl. Polyt. J., ccvi, 498).

The mother-liquor left in preparing saltpetre from the ash of beetroot molasses is mixed with saw-dust and deflagrated, the charred mass exhausted with water, the solution evaporated to 1·317 s. g., and the sulphates and chlorides allowed to crystallise out. This second mother-liquor is mixed with hydrochloric acid, heated, filtered from precipitated sulphur, &c.. and boiled with nitric acid till all iodine and bromine are expelled. The rubidium is now precipitated from the diluted solution by platinum tetrachloride, and separated in the usual way.

Direct experiment shows that one kilogram of the beet-ash of Northern France contains 1·75 grm. of rubidium chloride, and that the rubidium chloride is to the sodium chloride and potassium chloride as 1 : 126 and 331.

C. H. G.

Composition of Ultramarine. By W. MORGAN (Deut. Chem. Ges. Ber., vi, 24—25).

ULTRAMARINE contains, according to Unger, 5 per cent. of nitrogen, which is given off only on fusing the substance with ignited microcosmic salt or acid potassium sulphate. The author has repeated these experiments, but could not detect the least trace of nitrogen.

C. S.

Action of Magnesium Carbonate on Calcium Sulphate in Presence of Common Salt. By E. FLEISCHER (Journ. pr. Chem. [2], vi, 273—276).

WHEN a solution of calcium or barium sulphate is boiled with precipitated magnesium carbonate, these chlorides are almost completely converted into carbonates. Calcium sulphate is only partially decomposed, because on the one hand calcium carbonate decomposes some magnesium sulphate in a boiling solution, and on the other hand, calcium sulphate is less soluble in this liquid than in pure water. If, however, a hot solution of calcium sulphate be filtered through a large quantity of magnesium carbonate, the filtrate is almost free from calcium. This process appears to be a common one in the economy of nature. In the presence of common salt, the decomposition is more complete as calcium sulphate becomes more soluble, and the magnesium sulphate and sodium chloride decompose each other to magnesium chloride and sodium sulphate; but *large* quantities of the latter salt retard the decomposition of calcium sulphate.

C. S.

Preparation of Tellurium. By R. v. SCHRÖTTER (Chem. Centr., 1872, 434).

THE raw material is treated with dilute hydrochloric acid, as long as carbon dioxide is evolved, then with strong acid until all sulphuretted hydrogen is driven off. The liquid is decanted from the residue, which is washed with hydrochloric acid and hot water, then boiled with aqua regia until the insoluble matter is white. From the aqua regia solution any gold that may be present is precipitated by means of ferrous sulphate, and afterwards zinc is added to precipitate the tellurium. The precipitate on the zinc is washed, dried, and heated to redness, treated with sulphuric acid to remove any silver, and the remaining tellurium is then collected.

M. M. P. M.

On some Thallium Compounds. By S. M. JÖRGENSEN (J. pr. Chem. [2], vi, 82—91).

STRECKER found (*Ann. Ch. Pharm.*, cxxxv, 207) that the ammoniacal solution of a thallium oxysalt containing tartaric acid, gave with potassium iodide a black precipitate which contained no free iodine or nitrogen iodide, and was therefore regarded as an iodide.

The author's experiments lead him to the conclusion that the formula of this substance is $5TlI.TlI_3$. Several methods of preparing it are described, one of which, discovered by the author, is to dissolve thallious iodide with aid of heat, in a mixture of strong hydriodic acid and iodine. This solution, evaporated to dryness at 70°, leaves a blackish-grey crystalline precipitate, of metallic lustre, consisting of thallio-thallic iodide.

Cuprotetrammonium-thallium Iodide.—If to the reddish-yellow solution of thallious iodide in hydriodic acid and iodine, ammonia is added in slight excess, and this liquid is added gradually to a tolerably dilute, slightly warm solution of ammonio-cupric sulphate, a double salt is deposited, consisting of beautiful brown-red needles, often a centimeter in length. These when washed quickly in cold water, and dried over calcium chloride, have the composition $4NH_3.CuI_2.2TlI_3$.

Thallio-mercuric Chloride.—Carstanjen described this salt as consisting of $2TlCl.HgCl_2$. The author considered this improbable, and made fresh analyses, according to which the formula of the salt should be $TlCl.HgCl_2$.

Tetrethylphosphonium-thallium Iodide.—A hot alcoholic solution of tetrethylphosphonium iodide is mixed with potassium-thallium iodide, or with thallious iodide dissolved in an alcoholic solution of iodine. A crystalline precipitate separates, which, when dried at 108°, has the composition $P(C_2H_5)_4I.TlI_3$.

Tetrethylsulphine-thallium Iodide, $S(C_2H_5)_3I.TlI_3$.—Preparation and properties similar to those of the preceding compound. By means of this compound the author hoped to be able to establish an analogy between thallium and bismuth, and especially isomorphism between their double salts with iodine, but was unable to do so.

Tarconium-thallium Iodide.—Dark scarlet crystals are obtained from an alcoholic solution of tarconium tri-iodide (*J. pr. Chem.* [2], ii, 447), and hydrogen- or potassium-thallium iodide, corresponding to the phosphonium compound and having the composition $C_{12}H_{12}NO_3I.TlI_3$.

G. T. A.

Behaviour of Iodine and Sulphur towards Mercury.

By R. v. SCHRÖTTER (Chem. Centr., 1872, 531).

SULPHUR was placed in a barometric vacuum, and after some days it was found that mercuric sulphide was formed; if the action proceeded in the light, cinnabar was also produced.

Sulphur, iodine, and mercury act on one another, mercuric iodide being produced and the sulphur turned black. If a solution of iodine in potassium iodide be substituted for iodine, the sulphur remains unchanged, while all the iodine is taken from the solution, which becomes colourless, mercuric iodide being formed.

M. M. P. M.

Oxidation of Mercury.

By W. KIRCHMANN (Arch. Pharm. [2], cl, 203; and Chem. Centr., 1872, 517).

SHAKEN with potassium permanganate in the cold, mercury is oxidised to mercurous oxide; if heat be applied, to mercuric oxide.

M. M. P. M.

Fusion of Platinum in a Small Wind-furnace
By H. VIOLETTE (Compt. rend., lxxv, 1027—29).

THE flue of an iron wind-furnace, about a cubic meter in size, was inserted into the lower part of a brick chimney, 30 meters in height, which was in connection with several large furnaces, and through which therefore, when the furnaces were in operation, there was a strong draught. In the iron furnace, which was fed with coke, were placed successively Hessian, plumbago, lime, and Parisian charcoal crucibles, each containing 50 grams of iron nails. After an hour's heating, crucibles and metal were fused to a vitreous mass. Thinking the ash of the coke caused this fusion, the author next employed gas-carbon for fuel. The Hessian crucibles were still greatly injured, but by enclosing in a Hessian crucible another made from gas-carbon, he succeeded in preserving the metal intact. When 50 grams of platinum scrap and sponge were substituted for the iron, a button of melted platinum was obtained in less than an hour. (The Secretary of the Academy suggests that perhaps the platinum acquired traces of carbon, silicium, or sulphur during the operation, and thus had its fusion-point lowered.)

On repeating, in this arrangement, Ebelmen's experiment, which consists in forming crystallised alumina by prolonged heating together of alumina and borax, the author found the inside of the crucible completely covered with small, hard, translucent crystals of alumina. He suggests that precious stones might be thus artificially formed.

B. J. G.

Mineralogical Chemistry.

A New Method of Proximate Analysis of Minerals, and its Application to the Lavas of the last Eruption of Santorin.
By F. FOUQUÉ (Compt. rend., lxxvi, 1089).

THE mineral is reduced to a coarse powder, from which an electromagnet, excited by 6—8 Bunsen's elements, removes all the ferruginous, crystalline and vitreous particles, a white powder remaining behind, which contains nothing but the felspathic constituents of the mineral. If the powder be a mixture of fragments of different kinds of felspar, these may easily be separated by taking advantage either of their difference in size or of their different solubility in dilute hydrochloric acid. Besides this *mechanical* method of separation, the author employs strong hydrofluoric acid, in order to remove the felspathic and vitreous constituents. A white powder then remains behind, consisting of crystals of pyroxene, peridote, and ferrous oxide, the latter of which may be removed by a weak magnet. The crystals of pyroxene and peridote are sufficiently different in colour to allow of an easy separation with the aid of a magnifying glass.

By the combined use of the electro-magnet and of hydrofluoric acid, we are thus enabled to determine the relative proportions of the different crystalline constituents of certain minerals.

Applying his method to the lavas of the last eruption of Santorin,

the author proved them to contain albite, labradorite, and sometimes a little anorthite, besides a variety of pyroxene remarkably rich in ferrous oxide, also peridote, magnetic iron (?), and an amorphous substance differing in composition from albite only by a larger percentage of silica.

The nodules and the crystals found in cavities of the lava contain anorthite and varieties of pyroxene and peridote, different from those in the lava in which they are embedded.

R. S.

Stalagmitic Formations of the Solfatara of Puzzuoli.

By S. De Luca (Compt. rend., lxxvi, 357—359).

Stalagmitic formations exist on the level ground at the mouth of the great fumarole of the solfatara, just where the air meets the gases and vapours which are disengaged. They are fungiform, nearly cylindrical, with some prominences. Their upper surface is convex, nearly hemispherical, but slightly depressed. They are white throughout their substance. They have the composition expressed in the annexed table:—

Sulphuric anhydride	20·7
Sulphurous anhydride	3·6
Arsenious anhydride	1·5
Alumina	7·8
Lime	6·9
Ammonium oxide	5·3
Chlorine	1·5
Iron (ferrosum)	1·4
Silica	0·8
Water (loss at 100°)	27·8
Phosphoric anhydride, magnesia, potassa, soda, &c.	22·7
	100·0

Very small white stalactites are visible on the upper surface of the fumarole. The temperature here being much higher than on the floor, the stalagmitic matter can collect in a state of fusion, and then, falling drop by drop, solidify on the cooler floor of the fumarole.

E. D.

Bismuthoferrite. By A. Frenzel (Jahrb. für Mineralogie, 1872, 516).

A new and very pure specimen of this mineral has been found to have the following composition:—

SiO_2.	Fe_2O_3.	Bi_2O_3.	
24·05	33·12	42·83	= 100·0

These numbers place beyond doubt the fact that bismuthoferrite is a definite species. Hypochlorite is probably a mixture of bismuthoferrite, quartz, and another body of as yet undetermined constitution.

Hypochlorite and bismuthoferrite are distinguishable by their hardness

but not by their colour. The latter mineral occurs both in crystals and in finely granular, compact, and earthy forms.

W. F.

Pyrochlore from Schelingen, in the Kaiserstuhl Range.

By A. Knop (Jahrb. für Mineralogie, 1872, 534).

Nb_2O_5.	ThO_2 and CeO.	FeO.	MnO.	CaO.	Na_2O.	K_2O.	
61·90	10·10	1·80	0·40	16·00	7·52	4·23	= 101·95

W. F.

Nohlite, from Nohl, near Kongelf, Sweden.

By A. E. Nordenskjöld (Jahrb. für Mineralogie, 1872, 535).

This new mineral very closely resembles the samarskite from the Ural, but is distinguished from it by a rather considerable percentage of water. It is compact, of a black-brown colour, and is opaque and brittle. The fracture is uneven and splintery, and the lustre highly vitreous. The hardness is 4·5—5·0 and specific gravity 5·04 Before the blowpire it slowly melts at the edges to a dull glass, and feebly decrepitates through loss of water.

The analysis gave the following numbers:—

Nb_2O_5.	ZrO_2.	UO.	YO.	CeO.	CaO.	MgO and MnO.	FeO.	CuO.	H_2O.	
50·43	2·96	14·43	14·36	0·25	4·67	0·28	8·09	0·11	4·62	= 100·20

This composition accords approximately with the formula—

$$2R_6Nb_2O_5 + 3H_2O.$$

W. F.

Analysis of Arite, from the Mountain of Ar (Basses Pyrénées).

By F. Pisani (Compt. rend., lxxvi, 239).

Arite or Aarite is a nickeliferous mineral, associated with and intimately disseminated throughout a mixture of petrosilex, chalk, blende, ullmannite, and galena. It is amorphous, and has the colour of breithauptite. Density 7·19. Analysis gave the following results:—

S.	As.	Sb.	Ni.	Zn.	
1·7	11·5	48·6	37·3	2·4	= 101·5

The above numbers calculate to the formula $Ni_2(Sb.As)$, which is that of an arseniferous breithauptite. It would appear therefore that arite should be considered merely as a variety of breithauptite, in the same manner as the nickeline from Allemont, which contains 8 per cent. of antimony, is considered a variety of ordinary nickeline.

J. W.

Analysis of Jeffersonite, from Franklin, New Jersey.

By F. Pisani (Compt. rend., lxxvi, 237—238).

This specimen, having experienced no subsequent alteration, may be considered as typically representing Jeffersonite. It occurred in large

laminar masses, of more than one centimeter in thickness. It was translucent in thin layers, with a vitreous lustre, and broke with an unctuous but unequal fracture. Colour, deep green; hardness, 5·5; density, 3·63.

Before the blowpipe it melted to a slightly magnetic black enamel, and gave with sodium carbonate and nitre a strong reaction of manganese. It was unattackable by acids.

Analysis gave—

SiO_2.	Al_2O_3.	CaO.	MnO.	FeO.	MgO.	ZnO.	H_2O.
45·95	0 85	21·55	10 20	8 91	3·61	10 15	0 35 = 101 57

The oxygen ratio calculated from the foregoing numbers leads to the formula $\text{R}O.SiO_2$, and the mineral may be arranged in the group of pyroxenes. It is clearly distinguished from diopside and diallage by its geometrical and optical properties, and the details respecting these physical characters are given in the original communication. The percentage of zinc in the present specimen is much larger than that which has been recorded by previous analysts.

J. W.

Analysis of Lanarkite from Leadhills, Scotland.

By F. Pisani (Compt. rend., lxxvi, 114—116).

The mineral lanarkite was examined fifty years ago by Brooke, and more recently by Thomson. Both chemists agree in assigning to it the composition $PbSO_4 . PbCO_3$, giving, at the same time, as one of its chemical characteristics, that it is partially soluble in nitric acid *with effervescence*, leaving a residue of lead sulphate. The results of the author's examination of a great number of specimens of lanarkite, both from his own and from other mineralogical collections, lead to a different conclusion.

Not a single specimen effervesced when treated with nitric acid, and as a matter of fact it was observed that carbonic acid was invariably and entirely absent.

In order to guard against the possible substitution of anglesite for lanarkite, the crystallographic and general physical characteristics of the minerals were carefully studied. Upon these points, however, they agreed with those given by Brooke for lanarkite; but while the latter chemist obtained 7·3 per cent. of carbonic anhydride, the author could observe only 0·83 per cent. of loss on ignition, even when the mineral was heated to incipient fusion.

The following were the results of analysis—

PbO.	SO_3.	Loss.
82·73	15·10	0·83 = 98·66

These figures calculate to the formula $PbO.PbSO_4$, which is that of a basic lead sulphate. It is obvious, therefore, that the earlier mineralogists must have operated upon a different substance; at the same time it is scarcely probable that the mineral which they termed lanarkite should be so rare, that no collection in France should possess a single specimen.

J. W.

On a New Locality of Leadhillite. By E. Bertrand (Bull. Soc. Chim. [2], xix, 17—20).

The author's observations were made on some fragments of a mineral from Iglesias, in Sardinia, which agree exactly with the leadhillite of Lanark in Scotland, both in chemical composition and in optical properties. The coloured rings which they exhibit in polarised light show that the mineral belongs to the trimetric system; the optic axes are more divergent for the red than for the blue rays, the true dispersion of the axis being accordingly represented by the formula $\rho < \nu$. The apparent inclination of the axes in air is about 20° 30′ for natural light. The crystals are negative, the acute bisectrix coinciding with the axis of greater elasticity. All the Sardinian specimens exhibit a twin-formation of about 120°, like those from Leadhills. The hardness of the Sardinian mineral is between 2 and 3, rather nearer to 3; that of the Scotch mineral is 2·5. The density of the Sardinian mineral is 6·60 at 14°, which is rather higher than that of the Scotch variety, viz., 6·3 to 6·5, the difference being apparently due to alteration in the former, inasmuch as some parts of the Sardinian crystals are more or less opaque, contain water, and decrepitate when heated, whereas the perfectly transparent portions—which were selected for analysis—contain no water and do not decrepitate.

The mineral from Iglesias recently described by Laspeyres (p. 41 of this volume) under the name of maxite, is probably identical with leadhillite, agreeing exactly with the latter in its optical properties, and having a specific gravity of 6·874. The two minerals also do not differ greatly in chemical composition, as the following comparison will show.

	PbO.	CO_2.	SO_3.	H_2O.		
Leadhillite from Leadhills......	80·84	11·95	7·26	—	=100	(Stromeyer)
" " Sardinia (transparent)....	80·72	12·12	7·14	—	= 99·98	(Bertrand)
Maxite " "	81·91	8·08	8·11	1·87	=100	(Laspeyres)

The formula of leadhillite $3(PbO.CO_2) . (PbO.SO_3)$ requires 80·80 p.c. PbO, 11·95 CO_2 and 7·25 SO_3; that assigned to maxite by Laspeyres, viz., $5(PbO.SO_3) . (9PbO.CO^2) . (4PbO.5H^2O)$ requires 81·52 PbO, 8·08 CO_2, 8·16 SO_3 and 1·84 H_2O, which agrees exactly with his analysis. It is possible, however, that maxite may be merely leadhillite in which the alteration above noticed has taken place to a greater extent than in the Sardinian mineral.

H. W.

Crystalline Forms and Optical Properties of Amblygonite and Montebrasite. By A. des Cloizeaux (Compt. rend., lxxvi, 319; Proc. Roy. Soc., xxi, 174).

Both these minerals are triclinic. The author had previously found that the amblygonite of Montebras exhibits two cleavages inclined at an angle of 105° 44′ (p. 793 of the last volume). By examination of fresh specimens from the same locality, he now finds that the mineral cleaves in two other directions, making respectively with each of the

two former a very obtuse angle of nearly 152°. These four cleavages determine the faces of the primary parallelopiped $p\ m\ t$, or $0P. \infty'P. \infty P'$, or $001\ 110\ \bar{1}10$, having its right upper edge replaced by a truncation face i'. The angles of these faces are—

$$mt = 151° 4'; \ pm = 105° 44'; \ pt = 95° 20';$$
$$i'm = 96° 15'; \ i't = 95° 20';$$
$$pi' = 152° 57' \text{ (calc.)}, \ 152° 10' \text{ (obs.)}$$

Montebrasite from Hebron exhibits the three principal cleavages p, m, t, the angles between which are—

$$mt = 135° \text{ to } 136°; \ pm = 105°; \ pt = 89° \text{ to } 89° 11';$$

The angle pm is nearly the same in both minerals; but the other angles differ widely in the two.

In amblygonite the optic axes are situated in a place which divides into two very unequal parts the acute angle $pm = 74° 16'$. In the montebrasite of Hebron on the other hand, the plane of the optic axes is situated in the obtuse angle pm, and traverses the edge $\frac{p}{m}$, but is not quite normal to m, since it gives angles of 82° with m, and 23° with p. The character of the coloured rings shows that in montebrasite both from Montebras and from Hebron, there coexists with the horizontal a well marked inclined dispersion, and these are peculiar to the crystals of the triclinic system. In amblygonite from Montebras, the appearance of the bars traversing the central ring of each system indicates very distinctly a *twisted* dispersion which is also characteristic of the triclinic system.

The four-cleavage amblygonite has been analysed by Pisani with the following results:—

F.	P_2O_5.	Al_2O_3.	Li_2O.	Na_2O.	Loss by ignition.	
10·40	46·85	37·60	9·60	0·59	0·14	= 105·18

Its specific gravity is 3·076. It exhibits a commencement of kaolinisation, and imparts to the blowpipe-flame a red colour, less mixed with yellow than the lilac variety formerly analysed by Pisani.

H. W.

Examination of a Hepatic Limestone from Algeria.

By A. PETZHOLDT (Chem. Centr., 1873, 70).

THIS limestone, or marble, which occurs embedded in the granite, gneiss, mica-slate, and clay-slate of the mountain range near Fort Napoleon, has a coarsely crystalline structure, a white colour verging on blueish-green, and contains admixtures of quartz-crystals, mica, iron pyrites, and magnetic iron ore, visible in some parts to the naked eye, in others only to the microscope. Its cavities are lined with a thick layer of calc-sinter. When broken, or even when scratched with the point of a knife, it emits a strong odour of hydrogen sulphide. Analysis (by Korsaken) gave:—

$CaCO_3$.	$MgCO_3$.	Al_2O_3 and Fe_2O_3.	Insol. in HCl.	CS_2.
92·76	1·00	1·64	4·51	0·09 = 100

H. W.

Analysis of a Soil (Salt Earth) from the Primeval Forest of Brazil. By H. Ludwig (Chem. Centr., 1873, 69).

This soil is of a yellowish flesh-red colour, friable between the fingers, and has a greasy feel. Numerous laminæ of mica may be seen interspersed through it, even with the naked eye, appearing as irregular fragments under the microscope. No diatomes were found. Water extracted only a small quantity of sodium chloride, no nitrates. The soil boiled with soda-ley, gave a light yellow filtrate, which, when acidulated with hydrochloric acid, deposited after a while a few brownish flocks of humic acid. The analysis of the soil yielded the following results:—

	NaCl.	CO_2.	Na_2O.	CaO.	MgO.	Mn_3O_4.	Fe_2O_3.	Al_2O_3.	SiO_2.	
Sol. in HCl.	0·140	1·850	1·913	0·083	0·312	0·008	4·224	10·663	9·758 =	28·951
Insol. „ .	—	—	0·196	0·184	—	—	2·181	24·076	32·304 =	58·941
Water	—	—	—	—	—	—	—	—	—	12·900
										100·792

H. W.

Identity of the So-called "Unripe Amber" with Krantzite. By H. Spergatis (Wien. Acad. Ber., 1872, 200—202).

The similarity of the "unripe amber" which occurs associated with the amber of East Prussia to Bergemann's krantzite, has already been pointed out by the author (*Chem. Soc. J.* [2], ix, 893). The differences between the two in specific gravity, elementary composition, amount of ash, &c., are indeed not greater than those which are observed between two specimens of the one or the other, both these fossil resins being, in fact, mixtures of several compounds, and containing impurities unequally distributed.

H. W.

Gases enclosed in Coal. By E. v. Meyer (Journ. pr. Chem. [2], vi, 389—416).

The author has previously examined the gases contained in coal from Saxony, Westphalia, and from the Newcastle and Durham district, (see this Journal [2], x, 798 and 801), and he has now analysed the gases enclosed in coal from the Saar district. Ethene, which G. Bishof found, could not be detected, but the gases contain, besides marsh-gas, higher homologues, which were calculated as C_2H_6. The coal from the Gerhard pit is as hard and dense as Durham coal, and the gases con-

tained in it resemble in quality and quantity those enclosed in the latter. The following table contains the results:—

Locality and time when the coal was examined.	CO_2.	CH_4.	C_2H_6.	O.	N.	100 grams gave c.c. gas.
Kronprinz Pit.						
(A.) Wahlshied Seam.						
Gas blown out of a fissure	—	23·06	—	—	60·85	—
(mixed with air)	0	23·57	—	16·09	60·34	—
Air from the pit (where coal	1·25	2·39	—	17·77	78·59	—
had just been removed)	4·05	2·65	—	15·17	78·13	—
2 weeks....................	8·51	63·86	3·88	0·25	23·50	—
10 weeks....................	33·66	24·08	4·72	0·81	36·73	42·0
2 weeks....................	4·85	72·88	—	0·0	22·27	—
(B.) Schwalbach Seam.						
3 weeks	4·57	51·84	—	0·26	37·41	—
5—6 weeks....................	49·95	15·04		1·39	33·62	32·0
3—4 weeks....................	30·05	15·06	13·36	1·16	32·40	19·0
5 weeks	29·50	12·44	9·48	3·09	45·49	25·0
4 weeks	15·22	52·12	—	0·56	32·10	22·5
Geislautern Pit.						
No. 4 seam, 6 weeks............	19·19	37·94	3·22	0·97	38·68	26·0
No. 5 seam, 8 weeks............	35·66	9·46	3·61	2·63	48·64	21·2
No. 6 seam, 6 weeks............	26·12	55·65	—	1·20	17·03	53·0
Gerhard Pit.						
Fire-damp	0·62	22·52	—	14·01	62·85	—
Anna seam 4—5 weeks	trace	91·76	—	—	8·24	188·0
Sophie seam	1·83	90·79	—	—	7·38	158·0
Max seam	2·90	89·93	—	—	7·27	180·0

C. S.

Analyses of Four Mineral Waters of Bad Ems.

By R. Fresenius (J. pr. Chem. [2], vi, 53—78).

More than twenty years ago, in 1851, the author published the results of some careful analyses* of four different mineral springs at Bad Ems, on the River Lahn, and established by these analyses that the level of the river influenced the quantity of water which issues from these springs. The level having since undergone material alterations, he now records fresh analyses. The physical conditions under which the waters issue are carefully described, and the chemical results are given most minutely. They are, in fact, model analyses, such as we are accustomed to from this eminent analyst. For the details of the analyses, however, we must refer to the original paper,† and we quote merely the actual results, which may be compared with those obtained in 1851, by reference to the *Jahresbericht* of 1851, p. 652.

* "Chemical Examination of the most important Mineral Waters of the Duchy of Nassau; II, the Mineral Springs of Ems," by R. Fresenius.

† Published also in a separate form by C. W. Kreidel, Wiesbaden, 1872.

Composition per Litre. (The Carbonates are calculated as Anhydrous Bicarbonates, and the salts without their water of crystallisation.)

Names of Mineral Springs.	Kesselbrunnen.	Kränchen.	Fürstenbrunnen.	New spring.
Specific gravity	1·003028 at 17° C.	1·00308 at 16·9° C.	1·00323 at 16·9° C.	1·00300 at 17° C.
Temperature	46·64° C.	35·86° C.	39·42° C.	50·04° C.
Sodium bicarbonate	1·989682	1·979016	2·036607	2·052761
Lithium „	0·005739	0·004017	0·004439	0·005536
Ammonium „	0·007104	0·002352	0·002510	0·008215
Sodium sulphate	0·015554	0·033545	0·017060	0·041500
„ chloride	1·031306	0·983129	1·011034	0·927149
„ bromide	0·000454	0·000310	0·000350	0·000180
„ iodide	0·0000035	0·000022	0·000022	0·000004
„ phosphate	0·000540	0·001459	0·001167	0·000368
Potassium sulphate	0·043694	0·036773	0·018512	0·041151
Calcium bicarbonate	0·219605	0·216174	0·217019	0·220435
Strontium „	0·001815	0·002343	0·002477	0·001516
Barium „	0·001241	0·001026	0·001030	0·000981
Magnesium „	0·182481	0·206985	0·205565	0·210350
Ferrous „	0·003258	0·001989	0·001897	0·003985
Manganous „	0·000330	0·000173	0·000181	0·000334
Aluminium phosphate	0·000200	0·000116	0·000117	0·000209
Silica	0·048540	0·049742	0·049953	0·047472
	3·551546	3·519231	3·600240	3 565446
Free carbonic acid	0·930171	1 039967	1·029536	0·746261
	4·4817175	4·559198	4·629776	4·311707

The springs contain besides non-weighable quantities of—
Boric acid (combined with sodium), trace.
Cæsium and rubidium (combined with sulphuric acid), mere traces.
Fluorine (combined with calcium), trace.
Nitrogen, trace.
The second and third contain also faint traces of sulphuretted hydrogen.

W. V.

Water from the Springs of Partenkirchen. By G. C. WITTSTEIN (Chem. Centr., 1872, 521—522).

THESE springs are situated at a distance of 23 post miles from Munich. The water is clear, colourless, neutral, having a slight hepatic taste. The specific gravity at 12° R. is 1·000674; when the temperature of the air equalled − 1·25° R. that of the water was + 5·25 R. Analysis gave the following results:—

Parts per 1,000.

Potassium sulphate	0·043724	Lithium bicarbonate	traces
Sodium sulphate	0·054740	Ammonium "	0·009689
" thiosulphate	0·000489	Barium "	traces
" chloride	0·024710	Calcium "	0·117130
" nitrate	traces	Magnesium "	0·027809
" phosphate	0·002146	Ferrous "	0·001018
" bicarbonate	0·516584	Silicic acid (free)	0·012000
" bromide	traces	Carbon dioxide "	0·010042
" borate	traces	Sulphuretted hydrogen (free)	0·017885
		Organic matter	0·048437
			0·886403

M. M. P. M.

Organic Chemistry.

Note on the Polypropylenic Hydrocarbons. By M. PRUNIER (Compt. rend., lxxvi, 98—99).

IN studying the action of nascent hydrogen on propylene bromide by treating it with sodium amalgam, zinc and hydrochloric acid, and zinc and acetic acid, it was found that propylene was regenerated in all cases, but when acetic acid was used, the product obtained was sensibly less than with the other reducing agents; there was, moreover, considerable elevation of temperature. On submitting the product to fractional distillation, a viscous mixture of hydrocarbons was left, which was readily attacked by bromine, yielding a mixture of bromides. By fractional distillation the viscous mixture of hydrocarbons yielded a mobile liquid boiling between 70° and 80°, as well as one boiling between

330° and 340°. The latter was colourless, slightly viscous, and somewhat lighter than water; from its composition and properties it would appear to be hexpropylene $(C_3H_6)_6$, whilst the liquid boiling between 70° and 80° is probably dipropylene $(C_3H_6)_2$.

C. E. G.

On the Preparation of Propylene and Butylene Bromides. By L. Prunier (Bull. Soc. Chim. [2], xix, 109—111).

The author finds that these bodies and their homologues may be prepared in considerable quantities by passing the vapours of light petroleum oils through red-hot tubes, and leading the resulting gases through bottles containing bromine. The results vary with the kind of petroleum employed, the temperature of the tube, the pressure, and the rate of distillation. Petroleum oils boiling below 50° yield much ethylene and but little butylene; whilst oils boiling at 50°—80° yield butylene and even amylene, together with a considerable quantity of propylene and ethylene.

The most advantageous method of obtaining the propylene and butylene compounds consists in decomposing the vapours of petroleum oils boiling at 60°—90°, by passing them through a red-hot tube, and conducting the gases thereby produced through a second tube heated to dull redness, and afterwards through bottles containing bromine. The products are separated by fractional distillation, and decolorised by contact with quick-lime. There remain in the retort, together with carbonaceous matters, a crystalline body easily extracted by alcohol and ether, and having all the properties of Caventou's tetrabromide of crotonylene, $C_8H_6Br_4$, and another body which appears to have the formula $C_{10}H_8Br_4$, and which is still under investigation.

J. R.

Brominated Ether. By P. Schützenberger (Bull. Soc. Chim. [2], xix, 8—14).

Anhydrous ether combines with bromine, with evolution of heat, forming the compound $(C_4H_{10}OBr_3)_2$, a heavy garnet-red oil, which solidifies in a freezing mixture. The pure compound, obtained by draining off the liquid portion and recrystallisation, consists of brilliant plates resembling chromic trioxide, and melting at about 22°. It has a strong and irritating odour, but does not give off bromine at the ordinary temperature; it is very deliquescent and decomposed by water into its constituents. On keeping it for some time, it becomes liquid and gives off hydrobromic acid. When it is heated, ebullition begins at 80°, and hydrobromic acid and ethyl bromide are produced. By heating it in a water-bath in sealed tubes, it is resolved into water, hydrobromic acid, ethyl bromide, dibromaldehyde, bromal and tribromodialdehyde:

$$(1.)\ 2C_4H_{10}OBr_3 = H_2O + HBr + 3C_2H_5Br + C_2H_2Br_2O.$$
$$(2.)\ 3C_2H_2Br_2O = C_2HBr_3O + C_4H_5Br_3O_2.$$

Tribromodialdehyde, $C_4H_5Br_3O_2$, is a colourless, heavy oily liquid, boiling at about 175°, and possessing a strong and penetrating odour.

C. S.

Action of Zinc-ethyl on Silicium Methyl-ether.

By A. LADENBURG (Deut. Chem. Ges. Ber., v, 1081).

IN describing the products obtained by the action of zinc-ethyl on silicium ethyl-ether, the author has previously suggested the probability of the reaction being of the same kind as that which occurs when boric ether is acted upon by zinc-ethyl, and of its consisting in the removal of (OC_2H_5) groups from the ether and their replacement by (C_2H_5) groups derived from the zinc-ethyl.

Obviously this explanation might be regarded as demonstrated if it could be shown that by the action of zinc-ethyl on a silicium ether containing (OCH_3) groups in place of (OC_2H_5) groups, the former were capable of replacement by C_2H_5; if, for example, the first action of zinc-ethyl on silicium methyl-ether could be shown to take place as represented by the equation:—

$$2Si(OCH_3)_4 + Zn(C_2H_5)_2 + Na_2 = 2SiC_2H_5(OCH_3)_3 + Zn + 2NaOCH_3.$$

40 grams of silicium methyl-ether were therefore mixed with 24 grams of zinc-ethyl and 12 grams of sodium added gradually to the warmed mixture. By afterwards distilling and then fractioning the product, a liquid was obtained boiling at 125°—126°, which on analysis gave numbers agreeing well with the formula $SiC_2H_5(OCH_3)_3$. A vapour-density determination by Hofmann's method in toluidine vapour gave the number 146·9 as molecular weight, the calculated molecular weight being 150. This *orthosilicopropionic methyl-ether* is insoluble in water, and has a specific gravity of ·9747 at 0°; it closely resembles the corresponding ethyl-ether in odour and appearance, but is less stable. It is readily acted upon by hydriodic acid solution, and is also decomposed in contact with water, especially if ammonia be added, yielding silicopropionic acid. The author proposes to extend the method to the preparation of the homologues of silicopropionic acid, and announces the discovery of *silicobenzoic acid.*

H. E. A.

A New Tertiary Alcohol, and a Method of Preparing a Series of Tertiary Alcohols.

By C. FRIEDEL and R. D. SILVA (Compt. rend., lxxvi, 226—230).

THE authors find that pinacoline, $C_6H_{12}O$, prepared by heating pinacone with dilute sulphuric acid, and bearing the same relation to pinacone that ethylenic oxide has to glycol, yields, when treated with sodium in the presence of water, a white substance having the appearance of an alkaline alcoholate. This substance yields, on agitation with water, a liquid which, when distilled, passes over almost entirely at 120°, leaving in the retort a residue which crystallises on cooling. The liquid, which the authors call *pinacolic alcohol*, $\begin{matrix}(CH_3)_2COH\\ |\\ (CH_3)_2CH\end{matrix}$, is isomeric with hexyl alcohol. It has a camphorous odour, boils at 120·5°, and has a density of ·8347 at 0°. It solidifies at a low temperature to a

mass of long silky needles, which melt at 4°. By the action of iodide of phosphorus or hydriodic acid, it yields the *iodide* $C_6H_{13}I$, a liquid boiling at 140°—144°, and having a density of 1·4739 at 0°. Heated with water, it partly decomposes, with formation of a hexylene boiling at 70°. With silver acetate it yields the *acetate* boiling at 140°—143°, besides much hexylene. The *chloride*, $C_6H_{13}Cl$, obtained by the action of hydrochloric acid on the alcohol in closed tubes at 100°, boils at 112·5°—114·5°, and has a density of ·8991 at 0°. By careful oxidation of the alcohol with potassium dichromate and sulphuric acid, pinacoline is regenerated. Pinacoline itself, when submitted to oxidation, yields a volatile crystalline acid melting at 26°, which the authors are at present engaged in investigating.

The crystalline residue left in the retort after the removal of the pinacolic alcohol by distillation, melts at 69°, and is a pinacone of pinacoline:—

$$2C_6H_{12}O + 2H = C_{12}H_{26}O_2.$$

The molecular complication does not then stop at pinacoline, so that by starting from acetone it may be possible to obtain a series of these compounds by successive duplication.

C. E. G.

On Oxylepidene. By N. ZININ (Deut. Chem. Ges. Ber., v, 1104).

OXYLEPIDENE, $C_{28}H_{20}O_2$, melts at 340°, and is converted into two new modifications; one crystallises in rhombic plates, melting at 136°, and dissolving in 4·5 parts of boiling alcohol, and in one part of acetic acid.

Alcoholic potash converts it into the potassium salt of the acid $C_{28}H_{22}O_3$, which is insoluble in water, but dissolves in alcohol and ether. It forms four-sided prisms melting at 196°, and being resolved into water and oxylepidene.

The second modification dissolves in 76 parts of boiling acetic acid, but only sparingly in alcohol, and crystallises in octohedrons melting at 232°. The three oxylepidenes yield on dry distillation an isomeride of lepidene, $C_{28}H_{20}O$, crystallising from alcohol in square plates melting at 150°.

When rhombic oxylepidene is heated with phosphorus pentachloride and oxychloride to 180°—200°, *monochloroxylepidene*, $C_{28}H_{19}ClO_2$, is produced, which, from acetic acid, is obtained in crystals resembling tetrachlorobenzile and melting at 185°.

By heating equal parts of lepidene and phosphorus pentachloride until the excess of the latter is distilled off, *dichlorolepidene*, $C_{28}H_{18}Cl_2O$, is formed, which crystallises from acetic acid in needles, melting at 169°. *Dichloroxylepidene*, $C_{28}H_{18}Cl_2O_2$, is produced by heating lepidene with 4—5 parts of the pentachloride to 115°—120°; it crystallises in needles melting at 202°.

C. S.

Products of the Distillation of Sugar with Lime.

By R. BENEDIKT (Ann. Chem. Pharm., clxii, 303—308).

THE author confirms Frémy's results, that the two principal products are acetone and metacetone. He has further isolated an oily body which he calls isophorone, $C_9H_{14}O$, (the analyses quoted are not very concordant) having a vapour-density of 5·2 (calculated 5·05), and boiling at 208°—212°. This oil treated with anhydrous phosphoric acid gave a petroleum-like hydrocarbon, to which the formula C_6H_8 is assigned (C found = 88·3; calculated 90).

C. H. G.

Conversion of Cane Sugar into Glucose by the Action of Light.

By F. M. RAOULT (Ann. Chem. Pharm., clxii, 272, from Ann. Chim. Phys. [4], xxiii, 299).

TEN grams of white sugar were dissolved in 50 c.c. of water, the solution divided between two tubes—boiled for a few minutes and sealed up before air could re-enter; one tube was exposed to light, the other kept in darkness, but both were maintained at the same temperature. At the end of five months the tubes were opened—the solution which had been kept in the dark was unaltered—the other had had half its sugar inverted.*

C. H. G.

Hydracrylic Acid.

By J. WISLICENUS (Ann. Chem. Pharm., clxvi, 6—64).

BY treating a solution of β-iodopropionic acid with moist silver oxide, Beilstein obtained the acid $C_{12}H_{22}O_{11}$, which he called hydracrylic acid, because it is resolved by heat into acrylic acid and water. Moldenhauer found afterwards that when this acid is boiled with silver oxide, it is converted into a lactic acid, which, as Heintz believes, is ethene-lactic acid, whilst Socoloff regards it as an aldehyde of glycerin.

The author, however, has found that Beilstein's acid is not formed by the action of silver oxide on β-propionic acid, the chief product being a new isomeride of lactic acid, which he formerly called β-oxypropionic acid (this *Journal* [2], ix, 235), but for which he now prefers the name hydracrylic acid, because the name β-oxyproprionic acid has also to be given to ethene-lactic acid, from which, however, its isomeride differs by being completely resolved on distillation into acrylic acid and water, just as Beilstein's compound, which, if it does exist, will be a kind of anhydride of the new acid.

The product obtained by boiling an aqueous solution of β-iodopropionic acid with silver oxide was treated with hydrogen sulphide, and, after the excess of the latter had been expelled, neutralized with sodium carbonate and evaporated on a water-bath. The residue was then treated

* The abstractor of this paper has made many experiments in this same direction, and has invariably found that a solution of sugar (even when containing a trace of ammonia phosphate) remains *unaltered* by light, even after six months, if it be boiled vigorously for some minutes in a flask the mouth of which is stuffed with well baked cotton-wool.

with boiling alcohol of 95 per cent., which dissolves sodium hydracrylate, whilst the sodium salts of three other acids are left behind.

Sodium hydracrylate, $C_3H_5NaO_3$, is obtained generally in indistinct crystals or when the solution is very slowly evaporated, in small, flat prisms. It is very deliquescent, and very sparingly soluble in boiling absolute alcohol. When it is heated to 180° it loses one molecule of water, and is converted into a mixture of sodium acrylate and the isomeric paracrylate.

Zinc hydracrylate, $C_6H_{10}ZnO_6 + 4H_2O$. When a solution of this salt is evaporated on a water-bath a syrupy mass is left behind, which, when exposed to moist air, soon becomes crystalline, but by the spontaneous evaporation of an aqueous solution is obtained in large brilliant triclinic crystals. 100 parts of this salt dissolve at 16·5° in 89 parts of water.

Calcium hydracrylate, $C_6H_{10}CaO_6 + 4H_2O$, is also left as a syrup, when its solution is too far evaporated, but by adding a little water to the residue well-formed crystals are soon formed. It combines with the zinc salt, forming the double salt, $C_{12}H_{20}CaZnO_{12}$, which is but sparingly soluble in water. The silver salt, $C_6H_5AgO_3$, is readily soluble in water but not in alcohol, and forms slender prisms or needles.

Hydracrylic acid forms a strongly acid syrup, like lactic acid, from which it may be easily distinguished by being resolved by heat into water and acrylic acid, which, when heated with hydriodic acid, again yields β-iodopropionic acid. Oxidising agents convert hydracrylic acid into *carbon dioxide*, *glycollic acid*, and *oxalic acid;* carbacetoxylic acid seems also to be sometimes formed as an intermediate product, but neither acetic, glyceric, nor malonic acid is found amongst the product. By fusion with caustic potash it yields formic acid, acetic acid, and apparently a little glycollic acid.

When hydracrylic acid, or one of its salts, is heated with an excess of hydriodic acid in sealed tubes, it is converted into β-iodopropionic acid. Lieben's iodoform-reaction gives absolutely no result with hydracrylic acid.

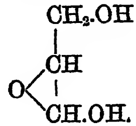
From the results of this investigation it follows that hydracrylic acid is neither an aldehyde of glycerin nor ethene-lactic acid, but is a new isomeride of lactic acid, of which four are now known, viz.:—(1) *common lactic* or *α-oxypropionic acid*, (2) *ethene-lactic acid*, (3) *paralactic acid*, which forms the chief constituent of sarcolactic acid, and has the greatest resemblance to common lactic acid, from which it differs by being optically active, and (4) *hydracrylic acid.*

Hydracrylic acid is very nearly related to allyl alcohol, acrylic acid, and acroleïn, and its constitution must be similar to that of these compounds, to which the following structural formulæ are now generally given:—

$$\text{Allyl alcohol}\ \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CH_2.OH. \end{array} \qquad \text{Acrylic acid}\ \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ CO.OH. \end{array} \qquad \text{Acroleïn}\ \begin{array}{l} CH_2 \\ \| \\ CH \\ | \\ COH. \end{array}$$

There can be no doubt that allyl alcohol does not contain the group,

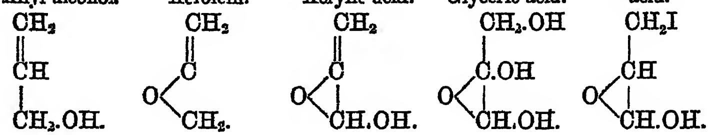
CH_3, which consequently cannot be present in acrylic acid, in its aldehyde, or in hydracrylic acid; and this is further proved by the fact that the latter acid neither yields acetic acid on oxidation nor iodoform by Lieben's reaction. Hydracrylic acid must therefore contain the group $CH_2.OH$, which does also exist in ethene-lactic acid, from which the former, however, differs by not yielding malonic acid on oxidation. Ethene-lactic acid also contains the groups CO.OH, which cannot be present in hydracrylic acid, or else the two acids would be identical, and therefore it appears very probable that the latter acid has the following constitution:—



A compound of this constitution would be an acid: for organic hydroxides are converted into acids, not only by transformation of the groups $CH_2.OH$ into CO.OH, but always when negative elements or radicals accumulate near an alcoholic hydroxyl.

If, therefore, this formula expresses the true constitution of hydracrylic acid, the compounds which are related to it must be constituted as follows:—

Allyl alcohol. Acrolein. Acrylic acid. Glyceric acid. β-Iodopropionic acid.

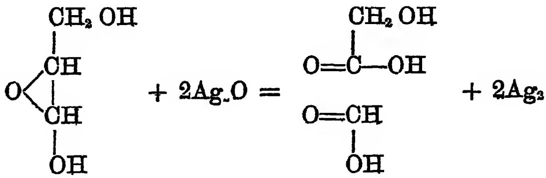


For the following reasons these formulæ appear to be more probable than those hitherto adopted. When an alcohol undergoes oxidation, the oxygen entering is attracted by that carbon-atom which is already combined with oxygen. Now in glycerin each atom of carbon is already combined with oxygen, and consequently the oxygen which replaces the hydrogen will be attracted as much by the first as by the second atom of carbon, and thus glyceric acid will have the above constitution.

Acroleïn, although possessing the general properties of the aldehydes, differs from all which have been carefully examined by not combining with the acid sulphites of the alkali-metals, and by being acted upon by ammonia in a totally different way. Further, the new formula explains, as well as the old one, its reduction to allyl alcohol and its oxidation to acrylic acid. When allyl alcohol is oxidised it again yields acrolein; in this case the oxygen is attracted, not only by CH.OH, but also by the second atom of carbon: for it is well known that when so-called non-saturated compounds are oxidised, the oxygen most readily attacks those carbon-atoms which are linked together by two combining units.

Hydracrylic acid is much more readily oxidised than any other modification of lactic acid; currents of carbon dioxide are given off, and at

the same time a strong smell of formic acid is perceived. The oxidation of hydracrylic acid therefore probably takes place in the following way:—

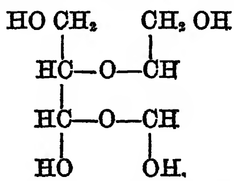


First formic acid and glycollic acid are formed, which are further oxidised to carbon dioxide and oxalic acid.

The formation of acetic acid, together with only a little glycollic acid, is not in contradiction to these views. Before the action of potash begins, a large quantity of hydracrylic acid will be converted into acrylic acid, which is resolved at a higher temperature into formic and acetic acids, whilst the glycollic acid is produced from some unaltered hydracrylic acid.

By the action of nascent hydrogen on β-iodopropionic acid, Moldenhauer obtained propionic acid. The author repeated this experiment, hoping to get an isomeride of common propionic acid, but the copper-salt which he prepared had all the properties of the salt of the normal acid. This may be explained by assuming that on removing the negative iodine, the oxygen is now more strongly attracted by the group CH.OH.

The molecular formula of hydracrylic acid is perhaps—



The existence of the sparingly soluble zinc-calcium double salt is in favour of this view. To decide this point, the ethyl-ether was prepared in order to determine its vapour-density. But this compound is completely destroyed by distillation, yielding bodies boiling partly below 100° and partly at a higher temperature, from neither of which could hydracrylic acid be reproduced.

C. S.

Acrylic Acid. By J. Wislicenus (Ann. Chem. Pharm., clxvi, 1—3).

Acrylic acid is completely converted into β-iodopropionic acid by heating it with concentrated hydriodic acid for three hours to 130°. On the other hand, when an intimate mixture of pure β-iodopropionic acid and lead oxide is distilled, acrylic acid is formed—

$$2C_3H_5IO_2 + PbO = 2C_3H_4O_2 + PbI_2 + H_2O$$

The acrylic acid thus formed has to be rectified once or twice over a little lead oxide to obtain it free from iodine.

C. S.

Lactophosphates. By R. Rother (Pharm. J. Trans. [3], iii, 570).

Lactic acid abundantly dissolves many of the insoluble orthophosphates when freshly precipitated; among the most prominent of the resulting combinations are the so-called lactophosphates of calcium and iron.

When lactic acid is treated with an excess of either of these phosphates in the cold, a solution is obtained, which still retains the acidulous taste of diluted lactic acid. If this solution is boiled, a copious granular precipitate occurs. If however it be not heated, but simply converted into a syrup by the addition of sugar, the saccharine solution, after the lapse of a few days, will deposit a voluminous white precipitate, or even completely gelatinise. The precipitates produced by heat or by time are again readily and completely soluble in hydrochloric acid, producing then a permanent solution. The precipitation is also completely prevented if the saturated phosphate mixture is heated with an additional portion of lactic or hydrochloric acid before precipitation has begun. The supernatant liquid from which the phosphate precipitate has spontaneously separated, apparently loses much of its acidity.

The general process for permanent solutions of the so-called lactophosphates is then as follows:—Take any convenient quantity of concentrated lactic acid, and saturate two-thirds of it with any desirable orthophosphate, freshly precipitated; then add the remaining one-third of the acid; and if the preparation is to be a syrup, dissolve the sugar in the solution without heat, and strain.

The following is the process for permanent syrup of calcium lactophosphate:—

Take of either the precipitated calcium phosphate, or calcined bones, about	6 drachms
Lactic acid (concentrated)	$1\frac{1}{2}$ troy ounces
Sugar	$10\frac{1}{2}$ troy ounces
Orange-flower water	2 fluid ounces
Hydrochloric acid, sp. gr. 1·16	1 troy ounce, or sufficient
Ammonia water	Of each sufficient.
Water	

Mix the hydrochloric acid with 1 fluid ounce of water, and add it to the powdered calcium phosphate, previously mixed with 4 fluid ounces of water. When the phosphate has dissolved, dilute the solution to 12 fluid ounces, and precipitate it with an excess of ammonia; pour the magma upon a filter, and wash it with cold water. Add this washed magma to the lactic acid, and, when dissolved, dilute the solution, after the addition of the orange-flower water, to $10\frac{1}{2}$ fluid ounces. Add the sugar to 9 fluid ounces of this liquid; stir frequently; and after most of it has dissolved, pour the syrup through a muslin strainer; mix the undissolved sugar with the remaining liquid; and after solution, add it to the rest of the syrup, through the strainer, and mix. J. B.

On some Reactions of Pyruvic Acid. By P. DE CLERMONT (Bull. Soc. Chim. [2], xix, 103—105).

1. WISLICENUS, by acting upon pyruvic acid with an equal number of molecules of bromine, obtained a crystalline compound, having the formula, $C_3H_4Br_2O_3$. This body is transformed into lactic acid by the action of sodium amalgam, and hence may be regarded as dibromolactic acid.

According to the author, this acid, when acted upon in the fused state by chlorine, evolves hydrochloric acid, and yields a product which crystallises from its aqueous solution in large, flat, rhombic crystals, efflorescent in the air and in a vacuum, and melting at about 93°. This product is free from chlorine, but contains bromine, and, notwithstanding discrepancies in analysis, the author believes it to be identical with the dibromopyruvic acid of Wichelhaus ($C_3H_2Br_2O_3$) with which it agrees in properties:

$$C_3H_4Br_2O_3 + Cl_2 = C_3H_2Br_2O_3 + 2HCl.$$

2. Pyruvic acid, heated to 100° for some time with hydrochloric acid in a sealed tube, undergoes decomposition, carbon dioxide being formed in abundance. The liquid yields on evaporation crystals having the composition of pyrotartaric acid, and melting at 110°—112°.

3. Sulphopyruvic acid, heated to 100° with aqueous solution of bromine in a sealed tube, yields a syrupy, non-crystallisable, brominated acid. Sulphopyruvate of barium, submitted to the same treatment, yields bromosulphopyruvate of barium, crystallisable, and soluble in water.

J. R.

Synthesis of a Diethyl Suberate. By C. HELL (Deut. Chem. Ges. Ber., vi, 28—32).

ERLENMEYER and the author have pointed out that active valerianic acid might possibly be *methyl-ethylacetic* acid. In order to decide this question the author heated pure ethyl monobromobutyrate* with methyl iodide and silver dust in closed tubes to 120°. But no ethyl valerate was formed, the products consisting of an inflammable gas (dimethyl), and a liquid boiling at above 200°. No better results were obtained by using ethyl moniodobutyrate. This ether is obtained by boiling an alcoholic solution of the bromobutyrate with potassium iodide in a flask connected with a reversed condenser. Ethyl moniodobutyrate boils, with partial decomposition, at 190°—192°. On heating it with silver and methyl iodide in a water-bath, the latter is not acted upon at all, the chief product of the reaction being, as in the case of the brominated ether, a liquid boiling at 233°—235°, and having the composition of *diethyl suberate.*

C. S.

* The pure compound boils constantly at 171°—172°, and not between 175°—185°, as stated by other authors.

Citric Acid and its Derivatives. By M. Sarandinaki (Deut. Chem. Ges. Ber., v, 1100).

Citric acid crystallises from a solution which has not been heated above 100° with one molecule of water, which it loses in the air, or more quickly at 130°. When the substance dried at 130° is re-dissolved in water, or when an aqueous concentrated solution of the acid is boiled for some time, anhydrous crystals are obtained, which the author regards as an isomeric modification of common citric acid. By heating normal ethyl citrate $C_6H_5(C_2H_5)_3O_7$, with alcoholic ammonia, to 70°—110° for 24 hours, *citramethane*, $C_6H_5(NH_2)_2(C_2H_5O)O_4$, is formed as a dark green amorphous and hygroscopic powder, which is soluble in water and alcohol, but not in ether, and is a colouring matter.

C. S.

Formation of Ketonic Acids. By E. Meyer (Deut. Chem. Ges. Ber., v, 1073—1075).

Calcium ethyl-oxalate was prepared according to the directions of Mitscherlich, and it was found that when this salt is crystallised it retains one molecule of water of crystallisation. Like the potassium salt, it yields ethyl-oxalate on distillation. When it is mixed with calcium benzoate and distilled, a distillate is obtained, which contains no ethers of ketonic acids, but ethyl-oxalate, ethyl-benzoate, and free benzoic acid. The formation of the latter was attributed to the presence of free oxalic acid in the calcium ethyl-oxalate employed, this view being confirmed by the fact that the distillation of a mixture of calcium benzoate with dry oxalic acid, yields a distillate containing benzoic acid and oxalic acid.

In order to throw light on this point, an intimate mixture of calcium ethyl-oxalate and chalk was distilled with calcium benzoate, and it was found that the distillate contained small quantities of free benzoic acid.

The author has in view the formation of ketonic acids by other reactions, such as the following:—

$$C_6H_5.CO.Cl + Cl.CO.OC_2H_5 + Na_2 = 2NaCl + C_6H_5.CO.COOC_2H_5,$$

or by replacing the CH_3 group in acetophorone by carboxyl.

T. B.

Derivatives of Acetone. By A. Emmerling (Deut. Chem. Ges. Ber., vi, 22—24).

Monobromacetone is readily formed by diluting acetone with 2—3 vols. of carbon sulphide, and adding a little less than the calculated quantity of bromine. After distilling off the carbon sulphide and excess of acetone, the product is left behind as a dark viscid mass. Freshly precipitated silver oxide in presence of water converts it into a volatile liquid, having a sweet taste, and reducing alkaline solution of copper salts. This compound, which appears to be the alcohol of pyruvic acid, could not be obtained pure, as it seems to be decomposed by dehydrating

bodies. Together with it, a smaller quantity of an acid, $C_{12}H_8O_{16}$, is formed, which in the free state forms a syrup having a sour and bitter taste, while the barium salt is a hard, amorphous mass.

C. S.

Reactions occurring in the Preparation of Carbon Monoxide from Potassium Ferrocyanide. By CARL JEHN (Arch. Pharm. [2], cl, 148; Chem. Centr., 1872, 516).

THE author considers it probable that the following equations represent what goes forward in the various stages of the action of sulphuric acid upon potassium ferrocyanide :—

(1.) $K_4FeCy_6 + 2H_2SO_4 = H_4FeCy_6 + 2K_2SO_4$.
(2.) $H_4FeCy_6 = 4HCy + FeCy_2$.
(3.) $FeCy_2 + H_2SO_4 = FeSO_4 + 2HCy$.
(4.) $6HCy + 12H_2O = 6(NH_4)CHO_2$
(5.) $6(NH_4)CHO_2 + 3H_2SO_4 = 3(NH_4)_2SO_4 + 6CO + 6H_2O$.

M. M. P. M.

On Hydrocyanides of Alkaloids. By F. A. FLÜCKIGER (Chem. Centr., 1872, 741).

THE author finds that, contrary to statements which have been published, the hydrocyanides of the organic bases cannot be prepared by double decomposition, or by the action of hydrocyanic acid on their alcoholic, aqueous, or alkaline solutions. The precipitates so obtained consist only of the pure bases.

W. A. T.

Action of Carbon Sulphide on various Amides, Aldehydes, and Alcohols. By HLASIWETZ (Chem. Centr., 1872, 532).

A. THE action of carbon sulphide on ammonia (in presence of a third body, which is itself unchanged) is to produce a crystalline colourless solid, having the composition $C_2H_{10}N_4S_3$, thus—

$$4NH_3 + 2CS_2 = C_2H_{10}N_4S_3 + H_2S.$$

B. By the action of weak oxidising agents this substance yields a solid crystalline body, $C_2H_4N_2S_4$, insoluble in cold water, but decomposed by boiling water into carbon sulphide, ammonium sulphocyanide, and free sulphur :

$$2C_2H_{10}N_4S_3 + Fe_2Cl_6 = C_2H_4N_2S_4 + 2NH_4CNS + 2NH_4Cl + Fe_2Cl_4.$$

C. Aniline yields, by the action of carbon sulphide, the corresponding salt $C_{14}H_{18}N_4S_3$. Boiled with water this substance is decomposed according to the equation—

$$C_{14}H_{18}N_4S_3 = \underset{\text{Sulphocarbanilide.}}{C_{13}H_{12}N_2S} + CS_2 + 2NH_3.$$

The relation of these three substances to one another and to biuret may be thus shown:—

$$
\begin{array}{cccc}
NH.NH_4 & NH_2 & NH.NH_3.C_6H_5 & NH_2 \\
| & | & | & | \\
CS & CS & CS & CO \\
| & | & | & | \\
S & S_2 & S & NH \\
| & | & | & | \\
CS & CS & CS & CO \\
| & | & | & | \\
NH.NH_4 & NH_2 & NH.NH_3.C_6H_5 & NH_2 \\
\text{A.} & \text{B.} & \text{C.} & \text{Biuret.}
\end{array}
$$

M. M. P. M.

New Mode of Formation of Methylamine. By C. VINCENT (Bull. Soc. Chim. [2], xix, 14—15).

CRUDE methyl alcohol, after being separated by distillation from the pyrologneous acid, is further purified by distilling it over lime. The portion passing over first has a strong alkaline reaction, and an ammoniacal smell, and contains a large quantity of methylamine. Greville Williams has already found traces of this base among the products of the dry distillation of crude calcium acetate.

The author has also found compound ammonias in impure samples of commercial wood-spirit, and in methyl nitrite prepared therefrom.

C. S.

Action of Iodine on some Hydrocarbons of the Aromatic Series. By P. SCHÜTZENBERGER (Compt. rend., lxxv, 1767—1769).

PURE benzene kept for 100 hours at 250° in sealed tubes with about 20 p.c. by weight of iodine, suffered little or no change. A small quantity of hydriodic acid was formed, together with a little black matter containing iodine and traces of a syrupy hydrocarbon; but nearly the whole of the iodine and of the benzene remained unaltered.

Naphthalene under the same conditions was completely broken up; hydriodic acid and a black iodized substance being the products of the reaction.

Toluene, however, gave more interesting results. After the heating there were found in the tube hydriodic acid and a small quantity of solid black matter. But the liquid in the tube, on being freed from iodine by agitation with potash, appeared fluorescent and greenish yellow. It was found to contain a number of hydrocarbons, which were separated by fractional distillation.

Benzene and xylene were found; probably due to the following reaction:—

$$2C_7H_8 = C_6H_6 + C_8H_{10}.$$

Toluene unaltered was found also in considerable quantity. These bodies passed over at 140°. Above that, the thermometer rose rapidly

and between 260° and 300° a thick oily hydrocarbon, which proved to be benzyl-toluene, was obtained, mixed with a small quantity of a more highly hydrogenated body. Analysis gave $C_{14}H_{15}$. The temperature rising, more liquid hydrocarbons came over, which were not recognised, but which gave on analysis numbers that corresponded to $C_{14}H_{13}$.

A solid red mass partly soluble in boiling alcohol was left in the retort, and the alcohol, on cooling, deposited a cinnabar-red mass, non-crystalline, and but little soluble in alcohol, but dissolving readily in benzene and carbon-chloride. Its analysis corresponded with the formula $2n(C_{14}H_{11})$. A substitution derivative was obtained by the action of bromine on it.

It appears from these experiments that iodine acts on toluene so as to remove hydrogen; and that condensed hydrocarbons less rich in hydrogen are obtained from its action.

J. T. B.

Pentachlorobenzenes. By A. LADENBURG (Deut. Chem. Ges. Ber., vi, 32).

THE author has lately shown that the existence of two pentachlorobenzenes is highly improbable. He has now investigated two samples of this compound which Otto had prepared, one melting at 224°—225°, and the other at 219°—223°. These bodies contain 74·39 per cent. and 74·06 per cent. of chlorine, from which it appears that both are nearly pure hexchlorobenzene, which melts at 225°, and contains 74·74 per cent. of chlorine.

C. S.

Compound of Azobenzene with Benzene. By G. A. SCHMIDT (Deut. Chem. Ges. Ber., v, 1106).

ON allowing a solution of azobenzene in benzene to evaporate, the compound $C_{12}H_{10}N_2 + C_6H_6$, crystallises in large transparent, rhombic oblique prisms. On exposing them to the air, benzene escapes, the crystals becoming opaque and friable, and consisting afterwards of an aggregation of small shining plates. In a closed tube the crystals melt at 38° to a dark red liquid, which solidifies after some time only. The same compound is also formed by acting with benzene vapour on azobenzene at the common temperature, but the compound itself still absorbs benzene, and at last a dark red solution is formed. Toluene does not combine with azobenzene.

C. S.

Synthesis of Phenyl-butylene. By B. ARONHEIM (Deut. Chem. Ges. Ber., v, 1068).

WHEN sodium is added to a mixture of benzyl chloride and allyl iodide in ethereal solution, an action soon commences which requires the heat of a water-bath for its completion. The fluid portion of the product, when fractionated in Linnemann's apparatus, yielded first diallyl and

then a portion passing over at 176°—178°, the substance remaining in the retort consisting principally of dibenzyl. The fraction distilling between 176°—178°, was found to consist of *phenyl-butylene*. It is a colourless aromatic oil, possessing an odour recalling that of unsaturated hydrocarbons. Its specific gravity is 0·915 at 15·5°, and its vapour-density was found to agree with the formula $C_{10}H_{12}$. The direct action of bromine on it occasioned the separation of hydrobromic acid, but by treating its solution in chloroform with bromine, the compound $C_{10}H_{12}Br$ was obtained as an oil distilling without change. The action of potash on this bromide caused the separation of hydrogen bromide, but the formation of a hydrocarbon, $C_{10}H_{10}$, was not established.

Oxidation with dilute nitric acid gave rise to the formation of an oil smelling like bitter almond oil, and a sublimable compound which appeared to be a mixture of benzoic acid and cinnamic acid.

The action of sodium on a mixture of benzyl-bromide and amyl bromide gave rise to capryl-benzene.

The author is continuing his investigations.

T. B.

New Synthesis of Anthracene. By A. van Dorp (Deut. Chem. Ges. Ber., v, 1070—1072).

When anthracene is formed by heating benzyl chloride with water, an oil is also produced which boils at 282°, and possesses, according to Limpricht, the formula $C_{14}H_{14}$. This compound, when passed over red-hot pumice, yields anthracene, and the author finds that when it is oxidised by chromic acid mixture, it yields the benzyl-benzoic acid recently described by Zincke. Thinking it probable that this oil consists of benzyl-toluene, the author prepared some of the latter substance, and found that it is decomposed when passed over red-hot pumice, anthracene being formed and hydrogen liberated—

$$C_{14}H_{14} = C_{14}H_{10} + H_4.$$

Hence he concludes that the oil described by Limpricht is benzyl-toluene.

If it be assumed that the benzyl-toluene used is a 1, 2 derivative of benzene, this synthesis of anthracene may be considered as confirming the second constitutional formula ascribed to this body by Graebe and Liebermann.

The author considers it probable that the hydrocarbon boiling at 270° and having the composition $C_{14}H_{12}$, which Berthelot obtained by passing toluene through a red-hot tube, is benzyl-toluene, and he also considers that the synthesis of anthracene from benzyl-toluene may be extended to the higher homologues. This is confirmed by the fact that he has obtained dimethyl-anthracene from xylyl-xylene. Possibly such bodies as ditolyl and hydrobenzoin may undergo a similar condensation.

T. B.

Compounds of Aldehydes with Phenols and Aromatic Hydrocarbons. By A. BAEYER (Deut. Chem. Ges. Ber., v, 1094—1100).

To study the action of formaldehyde, the acetate which Butlerow obtained by the action of silver acetate on methene iodide was employed. Methene iodide was prepared in the following way:—A litre-flask was connected with a reversed condenser, the upper end of which was provided with a T-tube; 200 grams of hydriodic acid and 50 grams of iodoform were then placed in the flask and boiled; at the same time small pieces of phosphorus were added through one limb of the T-tube, while the hydriodic acid formed escaped through the other limb. As soon as the brown colour of the liquid had completely disappeared, 100 grams more of iodoform and phosphorus were gradually introduced. The methene iodide was digested with silver acetate and glacial acetic acid at 100°, and the product, after distillation, rectified over silver acetate. The portion boiling between 130°—170° was either used as such, or after being heated with an equal weight of water for 6—8 hours to 100°. The latter liquid, which contains either the free aldehyde or the compound $CH_2{<}^{-OH}_{-OC_2H_3O}$, the author calls "aqueous methene acetate."

Aqueous methene acetate and hydrochloric acid yield with phenol a colourless resin, with pyrogallic acid a substance resembling tannin, and with resorcin an insoluble body burning like tinder. Gallic and salicylic acids give similar substances. The compound from gallic acid forms small colourless needles having the composition $C_{16}H_{12}O_{10}$.

When concentrated sulphuric acid is added to a mixture of methene acetate, benzene, and glacial acetic acid, an oil boiling from 260° to above 360° is formed, which consists of hydrocarbons.

Mesitylene gives a most characteristic reaction; by adding a cooled mixture of 10 parts of acetic acid and an equal volume of sulphuric acid to a solution of 1 part of mesitylene, 1 part of methene acetate, and 10 parts of acetic acid, and allowing the mixture, after shaking from time to time, to stand for 24 hours, large colourless crystals are formed, which, by recrystallisation from ether, are obtained in monoclinic prisms resembling cubes.

This body is *dimesityl-methane*, $CH_2(C_9H_{11})_2$. When heated it becomes soft, melts at 130°, and solidifies again at 62°. It is so readily produced, that its formation may be used as a test for mesitylene or for formaldehyde. The reaction never fails even if, instead of the pure aldehyde, a solution of methyl alcohol and chromic acid in glacial acetic acid is employed. When 2 parts of benzene and 1 part of chloral are mixed with an equal volume of sulphuric acid, *diphenyltrichlorethane*, $C(C_6H_5)_2H—CCl_3$ is obtained, crystallising from alcohol in small shining white plates, which melt at 64°, and solidify again at the common temperature. This reaction is quite a quantitative one, and chloral forms analogous compounds with other aromatic hydrocarbons.

The action of these aldehydes corresponds exactly with that of sulphur trioxide on benzene:—

$$SO_2.O + 2C_6H_6 = C_6H_5.SO_2.C_6H_5 + H_2O.$$
$$CH_2O + 2C_9H_{12} = C_9H_{11}.CH_2.C_9H_{11} + H_2O.$$
$$CHO.CCl_3 + 2C_6H_6 = C_6H_5.CH(CCl_3).C_6H_5 + H_2O.$$

C. S.

On Deoxybenzoïn. By SAGUMENNY (Deut. Chem. Ges. Ber., v, 1102).

THE compound, $C_{28}H_{26}O_2$, described by Limpricht and Schwanert, is most conveniently prepared by adding 1 part of deoxybenzoïn and 2 parts of zinc-dust to a solution of 1 part of caustic potash in 7 parts of alcohol, and applying gentle heat. The compound crystallises from alcohol to which a few drops of acetic acid are added, in needles melting at 164° and dissolving in 30 parts of boiling and 150 parts of cold alcohol of 90 per cent.; but on recrystallising it repeatedly from alcohol, the melting point is raised to 213°. Limpricht and Schwanert's compound melts at 156°, but after purification also at 213°. On distilling it, a portion volatilises and another is resolved into deoxybenzoin and stilbene hydrate.

C. S.

Dinitrobenzile. By A. SAGUMENNY (Deut. Chem. Ges. Ber., v, 1100).

WHEN benzile is treated with boiling fuming nitric acid, it yields two isomeric *dinitrobenziles*, $C_{14}H_8(NO_2)_2O_2$. One crystallises in octohedrons, melting at 131° and dissolving in 41 parts of boiling and 137 parts of cold alcohol, and the second forms plates, which melt at 147° and dissolve in 52·5 parts of boiling and 290 parts of cold alcohol.

C. S.

Pentabromoresorcin. By C. LIEBERMANN and A. DITTLER (Deut. Chem. Ges. Ber., v, 1090).

PARTLY on account of its physical properties the authors were inclined to regard the pentabromoresorcin prepared by Dr. Stenhouse as an additive compound of the formula $C_6HBr_3(OH)_2Br_2$, and not as $C_6HBr_5O_2$. In order to settle this question, they have determined the amount of bromine required to form it and the amount of hydrobromic acid produced, and have thus found that the reaction is correctly expressed by the equation—

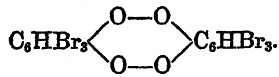
$$C_6H_4(OH)_2 + 5Br_2 = C_6HBr_5O_2 + 5HBr.$$

so that Dr. Stenhouse's formula is fully confirmed. But they are still inclined to regard it as an additive compound, on account of the following behaviour:—On heating pentabromoresorcin to 150°—160°, bromine is given off; and it was found by direct determination that the amount evolved corresponds to that required by the equation—

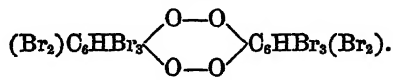
$$C_6HBr_5O_2 = C_6HBr_3O_2 + Br_2.$$

The residue, after washing with ether, is a crystalline yellow powder

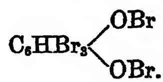
of the composition $C_6HBr_3O_2$, and may be appropriately termed *tribromo-resorquinone*, and represented as—

, or as 

Pentabromoresorcin may then be regarded as the additive compound—



The authors still admit, however, the possibility of the formation of tribromoresorquinone from a pentabromoresorcin of the composition—



H. E. A.

Frangulin and Frangulic Acid. By A. FAUST (Ann. Chem. Pharm., clxv, 229—236).

THE bark of the *Rhamnus frangula* is digested for three days with 90 per cent. alcohol at 25°—30°; from the extract the alcohol is partially distilled off, and then lead acetate is added to the residue as long as a precipitate falls: the filtrate from this is precipitated by basic lead acetate, and the precipitate disseminated through alcohol and decomposed by sulphuretted hydrogen; the resulting liquid yields crystals of frangulin on cooling after filtration while boiling hot.

Casselmann describes frangulin as crystallising under the microscope in quadratic tables; the author could not discern these tables either in his own preparation or in a specimen prepared by Casselmann, the two samples melting at 226° and 225° respectively, instead of 249° as stated by Casselmann. It forms a lemon-yellow crystalline mass after recrystallisation from hot alcohol, and is soluble in alkalis with a deep cherry red colour; when boiled with hydrochloric acid, it splits up into glucose and *frangulic acid:*

$$C_{20}H_{20}O_{10} = C_{14}H_8O_4 + C_6H_{12}O_6.$$

Hence the author ascribes the formula $C_{20}H_{20}O_{10}$ to frangulin, instead of the sub-polymeric formula $C_6H_6O_3$ attributed to it by Casselmann.

Frangulic acid is most conveniently prepared by boiling the bark with rain-water for an hour, then adding caustic soda equal to one-twentieth or one-thirtieth of the weight of bark taken, and boiling again for several hours: the resulting liquid extract is supersaturated with hydrochloric acid, and boiled for some hours, whereupon the frangulic acid separates and can be collected on a cloth filter; the dried and pulverised precipitate is boiled with alcohol, and the hot alcoholic solution precipitated by lead acetate (which scarcely precipitates frangulic acid); the filtrate is precipitated with basic lead

acetate, and the precipitate disseminated through alcohol and decomposed by sulphuretted hydrogen; and the resulting liquid is heated to boiling and filtered hot, the acid then separating from the filtrate on cooling. This treatment with lead salts, &c., is repeated several times; and the purified acid, after being dried and boiled with benzene to separate sulphur, is finally recrystallised several times from hot alcohol. Different samples of bark differ much in the quantity of frangulic acid obtainable from them; in one case, 50 lbs. yielded only a few grams.

Frangulic acid melts at 252°—254°, and sublimes partially at lower temperatures; it is but little soluble in hot water, and is insoluble in cold water and alum-solution: alkalis dissolve it, with a red colour, removed on boiling with zinc-dust; on treating it with red-hot zinc-dust anthracene is produced in small quantities; it crystallises with $1\frac{1}{2}$ proportions of water, the last $\frac{1}{2}H_2O$ being only removed at 180°.

Dibromo-frangulic acid, $C_{14}H_6Br_2O_4$, is obtained by adding bromine to an alcoholic solution of the acid; it is a clear light-red crystalline mass, difficultly soluble in cold alcohol.

Diacetyl-frangulic acid, $C_{14}H_6(C_2H_3O)_2O_4$, is obtained by heating the acid with an excess of acetyl chloride in sealed tubes to 130°—150°; it dissolves in about 300 parts of boiling alcohol, separating almost wholly on cooling as a crystalline mass of four-sided prisms, visible under the microscope; it melts at 184°, and when decomposed by caustic potash solution yields frangulic acid in its purest form. From these results frangulic acid appears to be isomeric with alizarin.

C. R. A. W.

On Curcumin. By Ivanow-Gajewsky (Deut. Chem. Ges. Ber., v, 1102).

The portion of oil of turmeric boiling at 280°—290° contains 80·2—80·4 per cent. of carbon and 10·8—10 per cent. of hydrogen; on oxidising it with chromic acid solution, it yields a mixture of acids, consisting apparently of valerianic and caproic acids. The lower-boiling portion of the oil contains more hydrogen and less carbon.

The best yield of curcumin is obtained by washing the ethereal extract of the root with weak aqueous ammonia, dissolving the residue in boiling concentrated ammonia, and passing carbon dioxide into the solution, by which it is precipitated into flakes. An alcoholic solution reduces silver nitrate, and an alkaline solution mercurous nitrate. The brick-red lead salt contains 43·6 per cent. of lead, corresponding to $C_{16}H_{14}PbO_4$. Curcumin heated with zinc-dust yields turmeric-oil boiling at 280°—290°, and by fusing it with potash protocatechuic acid is formed.

Rosocyanin is obtained by heating 100 grams of alcoholic turmeric-extract with 10 grams of boric acid and 30 grams of sulphuric acid on a water-bath. It is a crystalline purple powder with a green metallic lustre; it is insoluble in water but dissolves in alcohol. Traces of alkalis colour its solution dark-blue; it dissolves in sulphuric acid without decomposition, and contains 60·3—60·8 per cent. of carbon and 6·4—7·0 per cent. of hydrogen.

C. S.

On Camphoric Acid. By F. Wreden (Deut. Chem. Ges. Ber., v, 1106).

The nitration of the hydrocarbon, C_8H_{14}, obtained from camphoric acid (see this Journal, February, 1872,*) yields trinitro-isoxylene, from which it follows that camphoric acid is *tetrahydro-isoxylene-bicarbonic acid*.

C. S.

Sulphocinnamic Acid. By Rudnew (Deut. Chem. Ges. Ber., v, 1104).

By the action of fuming sulphuric acid on cinnamic acid two isomeric sulpho-acids are produced. The para-acid, $C_9H_8SO_5 + 5H_2O$, crystallises in large monoclinic prisms, and the acid barium salt, $(C_9H_7SO_5)_2Ba + 3H_2O$, in long needles; on fusion with potash it yields paraoxybenzoic acid. The second acid does not crystallise well; its acid barium salt, $(C_9H_7SO_5)_2Ba + 1\frac{1}{2}H_2O$, forms warty crystals, and is much more soluble than the para-salt. With potash it seems to yield oxybenzoic acid.

C. S.

Toluenedisulphonic Acid. By C. W. Blomstrand (Deut. Chem. Ges. Ber., v, 1084—1090).

This acid is prepared by heating toluenesulphonic acid, or one of its salts, with Nordhausen sulphuric acid at about 160°. The product is a mixture of two isomeric disulpho-acids, one of which, however, is obtained in small quantity only, its formation being favoured apparently by stronger heating (to about 180°).

Both appear to differ from the toluenedisulphonic acid obtained by Senhofer (this Journal [2], x, 1017) by heating toluene with sulphuric acid and phosphoric anhydride. The new acids are termed by the author α- and *β-toluenedisulphonic acid*, Senhofer's acid being distinguished as the γ-modification. The α-acid alone has been thoroughly examined. A number of salts of the acids are described, and also the following derivatives:—

α-Toluenedisulphonic chloride, $C_7H_6(SO_2Cl)_2$, crystallises from ether in large four-sided prisms, which melt at 51°—52°; the β-chloride is less soluble in ether, has apparently a different crystalline form, and melts at 94°. The *α-amide*, $C_7H_6(SO_2NH_2)_2$, crystallises in thin, long prisms, which melt at 186°; the β-amide is less soluble in water, and melts at about 216°. *α-Toluenedisulphydrate*, $C_7H_6(SH)_2$, and *α-toluenedisulphinic acid*, $C_7H_6(SO_2H)_2$, have been obtained, but not yet thoroughly examined.

Senhofer obtained salicylic acid and the so-called iso-orcin by fusion of his acid with potassic hydrate; the α-acid behaves similarly and

* In reply to a question asked in the above number of this Journal, the author says now (*Ann. Ch. Pharm.*, cxliii, 327), that his hydrocarbon is formed according to the equation—

$$C_{10}H_{16}O_4 = C_8H_{14} + H_2O + CO + CO_2.\text{—(C. S.)}$$

yields *salicylic acid*, together with small quantities of *paraoxybenzoic acid*, and an *orcin* which is evidently isomeric with ordinary orcin, and probably also with Senhofer's γ-orcin, although this is not definitively settled by the present experiments.

By fusion with sodium formate a small quantity of a *toluene-dicarboxylic acid*, $C_7H_6(CO_2H)_2$, was obtained from the α-disulpho-acid in the form of white, difficultly soluble flocculi, which exhibited signs of melting below 270°, but were at the same time carbonised.

On digesting the potassium salt of the α-disulpho-acid with chromic acid mixture, it is slowly oxidised and converted into *α-disulphobenzoic acid*, $C_6H_3(CO_2H)(SO_3H)_2$, which is certainly different from the acid obtained by Barth and Senofer (this Journal [2], ix, 828) directly from benzoic acid; it yields a highly characteristic, difficultly soluble acid potassium salt, $C_6H_3(CO_2H)(SO_3K)_2$ + aq., which is precipitated on the addition of hydrochloric acid to a solution of the normal potassium salt, $C_6H_3(CO_2K)(SO_3K)_2$ + 2aq.

The decomposition of this disulphobenzoic acid by potassium hydrate requires long-continued and strong heating, but takes place without the formation of by-products, and the resulting *α-dioxybenzoic acid* is at once obtained pure in an almost snow-white condition. This acid differs from Barth and Senhofer's (this Journal [2], ix, 828), which crystallises with $1\frac{1}{2}$ molecules of water and yields no coloration with ferric chloride, whereas α-dioxybenzoic acid contains either less or more water of crystallisation (either $1\frac{1}{2}$ or $2\frac{1}{2}$ molecules), and gives with ferric chloride a reaction closely resembling that of salicylic acid. It melts at 194°.

A number of other isomeric dioxybenzoic acids are known, but of these that obtained by Max Ascher (this Journal [2], ix, 827) is the only one which sufficiently resembles that above described to lend support to the view that the α-acid is identical with one of the dioxybenzoic acids already known. Ascher's statements of the properties of his acid are scarcely sufficient, however, to enable a decision to be arrived at on this point.

H. E. A.

Sulphuretted Tannic Acid from Phloroglucin. By H. SCHIFF (Deut. Chem. Ges. Ber., vi, 26—28).

By the action of disulphuric acid on anhydrous phloroglucin a crystalline sulpho-acid is formed, having undoubtedly the composition $C_6H_{12}\left\{\begin{array}{l}(OH)_3\\SO_3H\end{array}\right.$, inasmuch as phosphorous oxychloride converts it, like the isomeric sulphogallolic acid, into an anhydride, $C_{12}H_{10}S_2O_{11}$, a very soluble amorphous powder having an astringent taste and giving all the reactions of tannic acid. On boiling it with dilute acids it is again converted into sulphophloroglucic acid. This anhydride, is however, not the only product of the action of the oxychloride; but the other products were not obtained in a pure state.

C. S.

The Aromatic Amines. By V. Meyer and O. Stüber (Ann. Chem. Pharm., clxv, 161—188).

Most of the experiments described have formed the subjects of preliminary communications, and have already been noticed in this Journal.

Section 1.—In this portion reference is made to the rule laid down some time ago by one of the authors (V. Meyer, *Ann. Chem. Pharm.*, clvi, 265) that in the case of the chloro-, bromo-, iodo-, and nitro-derivatives of aniline and toluidine obtained by direct substitution, it is always the hydrogen directly contiguous to the amido-group which is replaced. In the case of the aniline derivatives this inference was based on the assumption that in quinone, and those bodies which may be referred to it, the side-groups are contiguous, whilst in the case of the toluidine derivatives it was based on the view that the members of the oxybenzoic series belong to the isophthalic series. Both of these views have recently been the subject of frequent discussion, and the latter, the authors believe, may now be regarded as definitively settled by the experiments of Ramsay and Fittig (this Journal [2], x, 491), and of Huebner and Jannasch (this Journal [2], x, 893). But the correctness of the former assumption has of late been several times challenged, and it is certain that conclusive evidence in its favour has never yet been obtained.

The authors have therefore sought further evidence bearing directly on this question. Thus they attempted to convert iodoaniline, by the action of sodium and carbonic anhydride, into amidobenzoic acid: potassium phenolsulphonate and anisolsulphonate were fused with sodium formate, the latter also distilled with potassium cyanide; phenolsulphonate was distilled with phosphorus pentachloride in the hope of obtaining a chlorobenzenesulphonic acid; and attempts were made to convert phenylenediamine (m. p. 140°) by Hofmann's method into a dicarboxylic acid—all these experiments, however, were failures.

It will be remembered that Ador and Meyer have converted sulphanilic acid both into resorcin and into terepthalic acid (this Journal [2], ix, 377); the authors have instituted a similar series of experiments with the isomeric acid produced by reduction of nitrobenzenesulphonic acid. They show that the acid obtained by heating nitrobenzene with sulphuric acid is a homogeneous product. It is stated that no odour of quinone is perceived on treating amidobenzenesulphonic acid with oxidising agents. Amidobenzenesulphonic acid is readily acted upon by nitrous acid; it does not, however, yield a diazo-derivative (like sulphanilic acid), but is converted into a diazo-amido-derivative. On treatment with hydrochloric acid, this latter gives a mixture of chlorobenzenesulphonic and amidobenzenesulphonic acids. The amount of product obtained by distilling the potassium salt of this chlorobenzenesulphonic acid with potassium cyanide was exceedingly small; it gave on treatment with alcoholic potash, &c., a small quantity of an acid, apparently isophthalic acid.

These experiments therefore still leave the constitution of quinone an open question, and the rule above referred to holds good for the aniline derivatives, only on the assumption that quinone is a 1 : 2 compound, and stands or falls with it.

Section 2.—Liquid dibromobenzene from dibromaniline (this Journal [2], x, 303).

Section 3.—Tribromobenzene from tribromaniline (*ibid.*, 305).

Section 4.—The three modifications of dibromobenzene (*ibid.*, 304).

Section 5.—The isomeric dibromanilines (*ibid.*, 303).

Section 6.—α-Nitraniline. All attempts further to nitrate this body were unsuccessful.

Section 7.—Action of nitrous ether on some amides (this Journal, x, 303). Amidotrinitrobenzene (picramide) is not acted upon by nitrous ether, even when heated with it in sealed tubes at 160°; on heating it to 200° a black tarry mass results.

H. E. A.

Nicotine. By H. WEIDEL (Ann. Chem. Pharm., clxv, 328—349).

ATTEMPTS to produce new compounds by treating nicotine with monochloracetic ether (which gives sarcosine with methylamine), phosphorus chloride, and acetyl chloride, and with nitrous acid (which, with conine, yields azoanhydrin, whence conyline is obtainable), proved unsuccessful.

When nicotine is dropped into 25 parts of well cooled fuming nitric acid contained in a capacious flask, a powerful reaction sets in when the temperature reaches 20°—25°, red vapours being copiously evolved; when this ceases, the whole is heated to boiling, until the liquid assumes a wine-yellow tint; the product is then evaporated to a small bulk on the water-bath, and set aside for some hours, whereupon crystals gradually form, and convert the whole into a magma, from which the fluid portion is extracted by a Bunsen's water pump; on treating this portion with more fuming nitric acid, a further portion of crystalline product is obtained.

The crystals contain nitric acid, even after two recrystallisations from hot water; they must, therefore, be converted into the silver salt by precipitation of the solution (neutralised with ammonia) by silver nitrate; the precipitate is decomposed by sulphuretted hydrogen, and the filtered solution allowed to crystallise. The product tastes strongly and purely sour, and is but little soluble in cold water, readily in hot water, and boiling alcohol, and insoluble or nearly so in ether. It sublimes perfectly; acts as a powerful acid, and (when neutralised) precipitates most metallic solutions. When heated with soda-lime, it yields a distillate, which boils at 115°—122°, exhibits the properties of *pyridine*, and has the composition of that base. The crystals contain no water of crystallisation, and have the composition, $C_{10}H_8N_2O_3$; the author terms the product *nicotic acid*. It appears, however, to be a kind of amido-acid, as it unites with strong acids, the crystals first obtained as above being a nitrate; a crystalline hydrochloride, sulphate, hydrolanide, and platinochloride are also obtainable, of the following compositions respectively:—

Nitrate	$2(C_{10}H_8N_2O_3) . 3HNO_3 . 3\frac{1}{2}H_2O$.
Hydrochloride ..	$2(C_{10}H_8N_2O_3) . 3HCl$.
Hydrobromide ..	$2(C_{10}H_8N_2O_3) . 3HBr$.

Platinochloride .. $2(C_{10}H_8N_2O_3) . 3HCl . 3PtCl_2(Pt=99 ?)$
Ditto, air dried .. $2(C_{10}H_8N_2O_3) . 3HCl . 3PtCl_2 + 4H_2O$.

The following salts have been examined and analysed :—

1st. Silver compound, indistinctly crystalline, formed by adding silver nitrate to the solution of the acid :

Dried at 110°...... $2(C_{10}H_7AgN_2O_3) . 3AgNO_3$.

2nd. Silver compound precipitated from the solution, saturated with ammonia by silver nitrate :

Dried at 110°...... $2(C_{10}H_7AgN_2O_3) . 3Ag_2O$.

Calcium compound, finely crystalline :

Dried at 120° $2(C_{10}H_7Ca'N_2O_3) . 3(C_{10}H_6Ca'_2N_2O_3)$
Air-dried .. $2C_{10}H_7Ca'N_2O_3 . 3C_{10}H_6Ca_2N_2O_3 . 19H_2O(Ca'=20)$

When treated with water and excess of bromine (5 parts of the latter to 1 of acid) nicotic acid splits up thus :—

$$C_{10}H_8N_2O_3 + H_2O + 11Br = C_5H_5N.HBr + 3CHBr_3 + 2CO_2 + N + HBr.$$

pyridine hydrobromide and bromoform being produced. Hydriodic acid of sp. gr. 1·57 produces no change in the nicotic acid, after several hours' boiling. Metallic-green crystals are formed on cooling, consisting probably of a kind of super-iodide; by exposure to air these become colourless, leaving the hydriodide of nicotic acid. Acetyl chloride has no action on nicotinic acid.

Hübner found that by oxidising nicotine with potassium dichromate and sulphuric acid, an acid was obtained, to which he gave the name *carbopyridic acid*, and attributed the formula, $C_6H_5NO_2$; when heated with alkalis, this acid yielded pyridine (*Deut. Chem. Ges. Ber.*, iii, 849); the author has repeated his experiments, and finds that the acid thus produced is really nicotic acid, $C_{10}H_8N_2O_3$. This formula differs from Hübner's only to a very small extent in the percentages of carbon and hydrogen contained, the nitrogen being 11·38 in Hübner's formula, and 13·72 in Weidel's. When treated with lime, the author finds that it is much nitrogen comes off as such, whilst carbon is deposited, and calcium carbonate formed. Hence the reaction is *not* that supposed by Hübner to take place, viz. :

$$C_6H_5NO_2 = CO_2 + C_5H_5N,$$

but is much more complicated, only half the carbon and nitrogen of the nicotic acid coming off as pyridine.

The synthesis of nicotine may not impossibly be effected by treating the aldehyde of pyrotartaric acid with ammonia :

$$2C_5H_8O_2 + 2NH_3 = C_{10}H_{14}N_2 + 4H_2O.$$

The author contemplates experiments on this point.

C. R. A. W.

Narceine Hydrochloride. By A. Petit (Bull. Soc. Chem. [2], xviii, 534).

Narceine hydrochloride, as met with in commerce, contains a variable quantity of hydrochloric acid associated with the base. When narceine is dissolved in excess of acid, and the whole evaporated to dryness, the hydrochloric acid retained is smaller in quantity the longer the evaporation has been continued; if the base is dissolved in just sufficient acid, the solution does not deposit crystals if more water than 50 parts to 1 of narceine be present; with 25 to 1, crystals are deposited, the formula of which is $\overline{N}.HCl.5HO$ $(O = 8)$; if 1 part of narceine be dissolved in 70 parts of dilute acid containing 3 grams to the litre mixed with 30 of water, crystals form on cooling, which have the composition $5\overline{N}.HCl$; whilst if 30 of this acid and 70 of water be employed, the crystals are $10\overline{N}.HCl$. This latter product is also obtained by the action of water on either of the hydrochlorides, $\overline{N}.HCl.5HO$, or $5\overline{N}.HCl$.

Narceine is very soluble in potash and in ammonia.

Narceine dissolves in		769	parts of water
Ditto + HCl	,,	277	,,
Ditto + 2HCl	,,	150	,,
Ditto + 3HCl	,,	130	,,
Ditto + 4HCl	,,	50	,,

C. R. A. W.

Oleate of Mercury and Morphine. By Charles Rice (Pharm. J. Trans. [3], iii, 582).

Although mercuric oxide is perfectly soluble in pure oleic acid, yet with commercial oleic acid, a portion of the mercury oxide is almost invariably reduced to the metallic state, the quantity reduced being in direct proportion to the temperature employed. To obtain a compound of uniform composition, the following process is recommended:—Expose the commercial oleic acid to a temperature of 40°—50° F., and express the liquid portion. Take of this prepared oleic acid, 1,536 grains; mercuric oxide, perfectly dry, 192 grains. Rub the oxide in a mortar with some of the oleic acid, to a smooth paste; add the remainder of the acid; place the mortar on a water-bath, and promote solution by frequently stirring, taking care not to allow the temperature to exceed 200° F.

As soon as the undissolved residue is of a pure grey colour, remove the mortar from the water-bath, and allow it to stand for 24 hours. Then pour off the clear solution into a tared capsule; wash the residue thoroughly with ether; and add the washings to the liquid in the capsule. Expose the latter to a gentle heat, until all the ether has evaporated, and weigh. The residue, after being washed and dried, without heat, may be weighed as metallic mercury, which is in practice sufficiently correct. Disregarding the small loss which occurs, suppose the weight of the solution obtained to be 1698 grains, and the weight of reduced mercury to be 30 grains. The 30 grains of mercury are equivalent to

32·4 grains mercuric oxide, and 159·6 grains (192—32·4) or 9·4 per cent., have therefore been dissolved.

Dissolve now 53 grams of morphine in 909 grams of oleic acid, and add the mixture to the above solution. The total quantity is now 2660 grains, and it contains 6 per cent. of mercuric oxide and 2 per cent. of morphine, which is the strength now deemed sufficient for most purposes.

Oleate of mercury and morphine is scarcely ever used for the purpose of producing the constitutional effects of mercury, but rather as a resolvent of articular anchylosis, and it has produced excellent effects in cases of chronic articular rheumatism and in gout, by removing the stiffness, and producing flexibility of the joint.

J. B.

The Active Principle contained in the Aqueous Distillate of Cantharides. By E. Rennard (Chem. Centr., 1872, 568).

Notwithstanding Radecki's statement that cantharidine does not volatilise with the vapour of water, the author finds that a considerable quantity of this substance passes over when it is distilled with water. Moreover he finds that cantharidine is to some extent volatile with the vapour of chloroform. When an old sample of cantharides (a portion of the sample used by Radecki) was distilled with water, no cantharidine was found in the distillate, cantharides which have been kept for a long time occasionally containing no cantharidine.

The aqueons distillate of cantharides contains not only cantharidine, but an animal oil having a low boiling point.

The solubility of cantharidine in the following solvents has been determined, the results being as follows:—

	Per cent. of cantharidine dissolved.
Boiling water	0·290 —0·297
Cold water	0·020
Boiling alcohol	2·030 —2·168
Cold alcohol	0·127
Boiling benzine	3·38
Cold benzine	0·51
Hot hydrochloric acid (sp. gr. 1·17)	0·3
" " "	0·137

T. B.

Alkaloïds from "Isopyrum Thalictroïdes." By F. A. Hartsen (Chem. Centr., 1872, 523).

The roots of this plant contain two alkaloïds.

1. *Isopyrine*, obtained by boiling the mashed roots with water, filtering, evaporating the liquid to a syrup, and precipitating with ammonia. This precipitate is then dried, and treated with ether, whereby the isopyrine is dissolved out. The alkaloïd has a bitter taste, and forms an amorphous salt with dilute hydrochloric acid.

2. *Pseudoisopyrine.*—The residue obtained by boiling the roots with water is digested with alcohol, the resulting liquid evaporated till all alcohol is removed, and ammonia added to the watery residue. By treating the ensuing precipitate with ether, another alkaloïd is dissolved out, which crystallises in stellate groups of needles. The two alkaloïds may, if present together in solution, be separated by adding very dilute hydrochloric acid and ammonium chloride, whereby pseudoisopyrine only is thrown down as chloride.

The alkaloïds have not yet been further examined.

M. M. P. M.

Iodized Albumin, and Iodized Albumin with Ferric Citrate.

By LUIGI GUERRI (Pharm. Trans. [3], iii, 644).

To investigate the action of iodine upon albumin, the latter was saturated with dilute phosphoric acid, and the liquid evaporated to 3° Beaumé. Finely divided iodine, obtained by precipitating tincture of iodine with water, was then added. This caused the albumin to turn red, but after some time it regained its primitive colour. Successive additions of iodine were made until the red colour appeared permanent, and starch paste was coloured blue. The liquid was agitated, and after ten or twelve hours, it once more regained its primitive colour, and no longer gave the reaction with starch, except under the influence of chlorine or nitric acid. On evaporation to dryness, the iodine still remained in combination with the albumin. Iodized albumin forms yellow transparent scales, soluble in water, with the exception of a few flakes which are insoluble in acetic or phosphoric acid, but soluble in alkalis. The solution is neutral, gives no iodine reaction, and is precipitated by alcohol. 100 parts of iodized albumin dried at 60° contained 3·132 parts of iodine; and 474 parts of the solution of albumin at 3° Beaumé, when so evaporated, yielded 31·928 parts of iodized albumin which contained 1 part of iodine.

To obtain a ferruginous preparation of the above strength, 18 parts of ferric citrate, corresponding to 5 parts of ferric oxide, were dissolved in 474 parts of iodized albumin of density 3° Beaumé, and the solution evaporated to dryness at 60°. This gave 50 parts of a compound containing one-third of ferric citrate and two-thirds of iodized albumin, and having the appearance of ferric citrate, but a little yellower. The solution comports itself like iodized albumin. The iron is not separated from it by alkalis, or by ferrocyanide of potassium, but is precipitated by the alkaline sulphides.

J. B.

Glutamic Acid. By H. HLASIWETZ and J. HABERMANN (Chem. Centr., 1872, 535).

THE authors have determined that *glutamic acid* may be prepared from animal proteïn substances by treating these with hydrochloric acid, and decomposing the product with silver oxide. Hitherto it was believed that this acid was obtainable only from vegetable proteïn.

M. M. P. M.

Stearoptene in the Flowers of "Clandestina rectiflora." By F. A. Hartsen (Chem. Centr., 1872, 524).

These flowers appear chiefly near the foot of the Pyrenees in early spring. The buds treated with ether yield two crystalline substances. The first substance is yellow and similar to cholesterin; the second is white, soluble in alcohol and ether, quite insoluble in water and dilute acids: it is called by the author *clandestinine*.

M. M. P. M.

Researches on Chlorophyll. By F. A. Hartsen (Chem. Centr., 1872, 524).

The author's researches show that a yellow crystalline substance very generally accompanies chlorophyll in the leaves of plants. This substance, called *chrysophyll*, is obtained by treating the leaves, previously freed from water by means of alcohol, with ethereal alcohol, pouring off the liquid after 24 hours' standing, and allowing it to evaporate spontaneously. Small crystals, having a gold-yellow lustre, are thus obtained (besides the chlorophyll); while still moist, the precipitate is treated with petroleum or boiling caustic potash, whereby the chlorophyll only is dissolved. The remaining chrysophyll is recrystallised from ether. The author considers it probable that this substance is identical with Frémy's *phylloxanthin*.

The green mass obtained by evaporation of the ethereal extract from leaves, yields with hydrochloric acid a greenish solution, from which, on addition of water, a black substance is precipitated. This substance the author calls *melanophyll*.

Chlorophyll is carried down from its solution together with many precipitates, as barium sulphate, calcium oxalate, silver chloride, &c.

The author is investigating a process for the preparation of pure chlorophyll.

M. M. P. M.

The Constitution of Suint. By E. Schulze (Deut. Chem. Ges. Ber., v, 1075—1078).

Cholesterin may be obtained from suint by saponifying it with alcoholic potash, mixing the product with water, agitating with ether, evaporating the ethereal solution and crystallising the residue from alcohol. The cholesterin thus obtained is mixed with an amorphous substance separating from alcohol in white flocks; it may, however, be freed from this body by several crystallisations from ether-alcohol.

When suint is treated with alcohol, about 10 or 15 per cent. dissolves, and this portion, when treated as above, yields a considerable quantity of cholesterin and only a small proportion of the substance separating in white flocks. This result renders it probable that a large proportion of the cholesterin of suint exists in the free state, its ethers being, with the exception of the acetate, very slightly soluble in alcohol.

That portion of the suint which remained undissolved by alcohol

yielded, when treated as above, a considerable quantity of the substance separating in white flocks and only a small proportion of cholesterin. To separate these substances, they were converted into benzoates, and these benzoates, when treated with alcohol and crystallised from ether, yielded shining rectangular leaflets and fine needles; these two kinds of crystals were separated by elutriation and crystallised from ether. The shining leaflets were then found to be cholesteryl benzoate, and the fine needles were found to be the benzoate of an alcohol which crystallises from acetone or ether in needles, and separates from alcohol in flock or jelly-like masses. This substance is still under investigation. T. B.

Physiological Chemistry.

Decomposition of Albuminoïds by Baryta. By O. Nasse (Chem. Centr., 1872, 721).

When albuminoïds are boiled with barium hydrate, a small fraction of the nitrogen is evolved as ammonia, the rest remaining as leucine. The percentage of the total nitrogen evolved, is from casein 17, serum albumin 19, fibrin 20, glutin 30. The syntonins prepared with weak (·4 per cent.) hydrochloric acid evolved, in the case of blood albumin 16, muscle 18, and egg albumin 21 per cent. of their total nitrogen. Of syntonins prepared with fuming hydrochloric acid, that from casein evolved 11, from blood albumin 18, and from glutin 24 per cent. of its nitrogen. Gelatin gives off 10 per cent. of its nitrogen when boiled with baryta. R. W.

On the Coagulation of Casein by Rennet, and on the so-called Amphoteric Reaction. By W. Heintz (Journ. p. Chemie [2], vi, 374—384).

This paper is a reply to some of the statements made by Soxhlet in his contributions to the physiological chemistry of milk (*vide* this Journal, N.S., vol. xi, p. 187). In regard to the amphoteric reaction described by Soxhlet as manifested by solutions containing both acid and neutral sodium phosphate, Heintz shows that in reality both red and blue litmus paper are coloured violet, but the violet has a redder tinge in the red paper, and a bluer tinge in the blue paper. Hence Soxhlet's view that both salts possess their individual acid or alkaline reaction in presence of each other seems untenable. Heintz supposes that the amphoteric reaction is due to the existence of a violet acid salt of the litmus which is produced when red or blue litmus solutions are mixed with salts which can give up part of their base or add to it.

Such a mixture of salts is formed by acid and neutral sodium phosphate. With reference to the statement of Soxhlet that the coagulation of casein by rennet is in all cases due to the development of lactic acid by the action of rennet on milk-sugar, Heintz brings forward the results of fresh experiments to show that coagulation of casein may be caused by rennet without the intervention of lactic acid. He even

denies that rennet possesses any influence in converting milk-sugar into lactic acid. D. F.

On the Peptic Action of the Pyloric Glands. By v. WITTICH (Pflüger's Archiv. f. Physiologie, vii, 18—27).

v. WITTICH has made experiments which seem to prove that the pyloric glands of the stomach do not possess the power of converting albumin into peptones. He determines the digestive action of the mucous membrane of the stomach by the rapidity with which a glycerin extract of the same dissolves a given quantity of swollen and acidified fibrin placed on a filter. The extract is made by steeping the mucous membrane in absolute alcohol, drying over sulphuric acid, and then extracting it with glycerin. Comparative experiments with the extracts made from the pyloric portion of the rabbit's stomach, and the fundus respectively, showed that the latter caused rapid solution and filtration of a given quantity of fibrin, while the former had little or no effect. Similar experiments with the pyloric and fundus extracts of the pig's stomach gave like results. In this case the mucous membrane was divided by a razor into superficial and deep strata, and comparative experiments were instituted as to the activity of each. The extract of the pyloric mucous membrane, superficial or deep, had little or no effect on fibrin, while that of the fundus was very active, but more especially the extract of the deeper portions. This tends to show that it is the so-called peptic cells which generate the pepsin. This is in opposition to the recent view of Herdenhain, who thinks that it is the other cells of the follicles which chiefly yield the ferment.

D. F.

The Liver Ferment. By v. WITTICH (Pflüger's Archiv., vii, 28—32).

IN reference to Tiegel's statements that the blood-corpuscles when undergoing disintegration in the liver yield a ferment which converts starch into sugar, v. Wittich shows that even serum alone may yield such a ferment by extracting the alcoholic precipitate with glycerin. He also obtains a diastatic ferment from the parenchyma of the liver when it has been quite freed from blood. It is difficult to obtain it quite free from sugar, but he shows that the glycerin extract when in contact with starch-paste, produces a very much larger quantity of sugar than may have existed in the extract.

This extract was prepared from a calf's liver, through the vessels of which a stream of water had been directed for four hours, the water coming through perfectly colourless, but still containing traces of sugar. When the liver was washed still longer, the water which poured from it contained no sugar, but when the process was interrupted for an hour, sugar again appeared. The liver so treated still yielded to glycerin a diastatic ferment. The ferment seems to be formed in the liver cells. It is partly poured out along with the biliary constituents, for as the author has shown, the fresh bile contains a diastatic ferment. D. F.

Origin of Indican in Urine. By Jaffé (Zeitschr. anal. Chem., xi, 358—359).

The author has made the interesting observation that after the subcutaneous injection of indol (prepared by Baeyer's method), very considerable quantities of indican constantly appear in the urine. The elimination of the latter body begins a few hours after injection, and generally ceases within 24 hours. Kühne has shown that indol is one of the products of the pancreatic digestion, so that Jaffé's previous conjecture that the indican of urine is partially, at least, derived from this source, appears to be verified. The indol of the intestinal canal is, for the most part, ejected with the fæces, imparting thereto its peculiar odour; a small portion is absorbed and reappears in the form of a conjugated compound, indican, in the urine.

J. R.

On Ammonia in the Urine in Health and Disease. By C. Meymott Tidy and W. Bathurst Woodman (Proc. Roy. Soc., xx, 362—365).

The authors refer to the researches of Andrews, Clark, Neubauer, and Vogel, and others, on the presence of ammonia as a constant constituent of healthy urine. Neubauer believed 7 grams per diem to be the average normal excretion. After numerous experiments, the authors regard this quantity as excessive, and suggest some reasons for this discrepancy.

The method adopted by the authors was as follows:—The freshly passed urine was first diluted with a given bulk of water, sufficient to destroy all apparent colour, a known quantity of the urine being taken in each case. To this was added an excess of Nessler's solution, and the colour thereby produced was compared with the tint-depth produced by known quantities of ammonia in a similar bulk of liquid treated with the same Nessler's solution. The trace of ammonia in the water itself was allowed for; but it is not stated that any precautions were taken to ascertain the influence of urinary ingredients, other than ammonia, upon Nessler's solution, nor that the tint due to urine-pigments was allowed for.

I. Ammonia in health.—The authors conclude that the average daily excretion of ammonia in health amounts to rather less than 2·5 grains, or 0·162 gram in 24 hours. The range of secretion was, however, a very wide one. The modifying results of age, sex, food, exercise, and atmospheric conditions are stated.

II. Ammonia in disease.—Before dealing with special diseases, the authors examined the influence of some general conditions both of the urine and of the patients. These general conditions were, the colour and the specific gravity of the urine, the pulse, respiration, temperature of the body, condition of the skin, tongue, and bowels, also diet, and medicines. The influences exerted by these modifying conditions upon the excretion of ammonia are stated.

Finally, the influence of special diseases is adverted to, and the results stated.

In erysipelas, small-pox, enteric fever, and typhus fever, the amount of ammonia excreted in 24 hours was found to be less than a fourth of the normal amount; in acute rheumatism and in phthisis rather more than two-thirds; in nervous diseases rather more than half; in diabetes and rheumatic gout, greatly in excess; nine cases of complicated disease with extreme physical prostration, showed a vast decrease in the amount of ammonia, and in two cases it was entirely absent.

The authors refrain from any generalisation. The total number of cases upon which observations were made exceeded 200.

T. S.

On the Structural Composition of Urinary Calculi.

By H. VANDYKE CARTER (Proc. Roy. Soc., xx, 81—83).

MINUTE fragments, taken from the real or apparent nuclei, and from succeeding layers and crust of the calculi, were submitted to the scrutiny of average optical powers. Water was the ordinary medium employed, and in all cases chemical tests were conjointly used for the purpose of detection or confirmation.

Particular attention was given to the nature of the nuclei or first-formed ingredients of the calculi, and the presence of urates in a globular form at their earliest beginning, was found to be very frequent. The next most common ingredient of the nucleus is calcium oxalate, in large rhombic crystals; frequently, however, octohedral, oval, and dumb-bell forms are seen, as well as spheroïdal bodies originating from the latter. The nucleus of a calculus was comparatively seldom found to consist of uric acid crystals.

The operation of known physical influences in determining the form which the salts assume in connection with stone, was investigated. Reference is made to the modifying influence of a colloïd medium upon the process of crystallisation; and it is here found that both urates and oxalates may present the various stages of globular particles, complex globules, or spheroids, either separate or blended, and laminæ of various thicknesses; there are evident signs, too, that these structures undergo, at times, more or less complete disintegration, which may be followed by a re-arrangement of their molecules, and more especially does the calcium oxalate seem disposed to undergo these changes, the resulting forms being highly characteristic. Neither uric acid nor the phosphates were found otherwise than in a simpler crystalline form; the former, however, when potassium hydrate is added, may in combination be noticed to pass into minute globular particles, the potassium urate being seen to assume some of the characters of ordinary urates; calcium phosphate artificially produced was also observed in the shape of dumb-bells and spheres. It is concluded that urinary calculi should not be classed with ordinary concretions or pure mineral masses.

The full paper, in the *Philosophical Transactions*, contains a description of each well-known ingredient as it was observed to occur, illustrated by plates showing the microscopical appearances of the specimens.

T. S.

Proportion of Phosphoric Acid to Nitrogen in Milk. By Stohmann (Chem. Centr., 1872, 722).

Meyer had remarked that in the grain of cereals the phosphoric acid and nitrogen are in the proportion of $P_2O_5 : 2N$; the author finds that these substances bear the same proportion to each other in goat's milk.

R. W.

Experimental Modifications of the Composition of Bones, II. By F. Papillon (Compt. rend., lxxxv, 352—355).

By appropriate dieting, the author has succeeded in getting small quantities of magnesium salts taken up by the bones of pigeons and chickens and by the so-called *eyes* of crabs. Comparing his experiments given in this paper with his previous experiments upon strontium and aluminium salts, he concludes that metals are assimilated in the proportion of their atomic weights. It must be added, however, that his numbers afford but little support to this view, even on his own method of calculation, which is erroneous fundamentally and in detail,—ratios of quantities of oxides being equated against ratios of the atomic weights of the metals,—Al_2 being placed with Mg as corresponding quantities, recognised as such by chemists, and the numerical value of Al_2 being given as 45 instead of 55 (54·8).

E. D.

Influence of Ethyl Alcohol on Animal Heat. By C. Binz (Deut. Chem. Ges. Ber., v, 1090).

The administration of alcohol does not increase the animal heat; after small doses the thermometer does not indicate any unusual rise or fall; larger doses, which need not, however, be sufficient to cause intoxication, lead to a perceptible fall of about 5° of short duration; quantities sufficient to produce intoxication cause a fall of as much as 2°, lasting several hours. The fall in temperature, after the administration of medium doses, takes place, in the case of warm-blooded animals, only in subjects which for some considerable time before have not taken alcohol. If accustomed to it, the organism is not affected either way by such doses; this, in the author's opinion, is the reason why Dr. Parkes noticed a constant temperature of the blood in all his experiments, the single subject employed by him being a soldier accustomed to the daily use of spirit.

As causes of the decrease of temperature, the author recognises the following:—(1.) The increased loss of heat from the outer surface of the skin, owing to the [illegible]tension of the blood-vessels and increased evaporation; (2.) The p[illegible]ative influence exercised by the alcohol on the chemical activity of t[illegible]l

H. E. A.

Assimilation by Sheep of Various Ages. By E. WOLFF (Chem. Centr., 1872, 724).

THE period of life experimented on was from the age of six to fourteen months. Some of the sheep were fed on meadow hay, others on hay and oats; the author determined the proportion assimilated of all the principal ingredients of the food. There was no evidence of any alteration in these proportions as the animals advanced in age.

R. W.

Feeding Experiments with Sheep. By F. HEIDEPRIEM (Landwr. Versuchs. Stat., xvi, 1—40).

Two 3-year old merino wethers were fed, during five consecutive periods of sixteen days each, as follows:—During period I each sheep received daily 1,000 grams of lupine hay; II, 500 grams of lupine hay and 1,000 grams of lupine straw; III, 1,250 grams of lupine straw; IV, 1,000 grams of lupine straw and 70 grams of seeds; V, 900 grams of lupine hay and 70 grams of seeds. The straw and hay were given as chaff and the seeds soaked in water; each animal also received 10 grams of salt daily.

The food had the following percentage composition:—

	Lupine seeds	Straw.	Hay.
Water	10 07	10 ·34	9 ·11
Sand	·17	·16	6 ·26
Salts	3 ·36	3 ·08	4 ·12
Albuminoids	43 ·35	6 23	23 ·53
Fat	3 ·87	1 ·10	1 ·99
Fibre	13 ·33	43 ·46	25 ·56
Non-nitrogenous extractive matter	25 ·85	35 ·63	29 ·13

During the last eight days of each period the food left unconsumed and the excrements were collected and analysed. The amount of water taken by each animal was also noted.

The principal results are given in the following table:—

Period	Sheep.	Dry food consumed in 8 days.	Dry dung.	Total percentage of dry food digested.	Percentage of constituents of the food digested. Albuminoids.	Fat.	Fibre.	Non-nitrog. extract.	Mean live weight. Kilos.
I.	1	5545·9 hay	2041 2	63·5	73·0	15·5	67·1	57 3	33·2
	2	4921 3 hay	1391 5	71·7	75·7	45·3	79·8	65·9	34·8
II.	1	2564·7 hay 6338 3 straw 8903·0	3693·1	58 5	54·1	18·7	53·6	68 7	37·8
	2	1147 6 hay 3588 0 straw 4735 6	1987·0	58·0	55 9	25 7	56 2	63·4	38·4
III.	1	8030·7 straw	3549·9	55·8	39·7	25·4	52·0	65·4	39·1
	2	7418 0 straw	3405 2	54·1	35·4	35·0	49·2	64·5	39·1
IV.	1	6769 8 straw 502 7 seed 7272·5	3108·7	57·3	48 9	39 6	54·0	65·1	37·8
	2	6810·5 straw 502 7 seed 7313·2	3275·4	55·2	49·0	44 1	47·7	67·0	39·5
V.	1	5795 3 hay 502·7 seed 6298·0	1909 0	69 7	77·1	36·3	68 8	70 7	34·5
	2	5187 9 hay 502·7 seed 5690·6	1167·3	70·5	77 9	12·9	63·7	75·8	35·7

The fibre and the albuminoids of the hay were digested to a considerably larger extent than these constituents in other similar foods. In all cases more non-nitrogenous extractive matter was digested than corresponds to Grouven's formula. The observed digestibility of the mixture of hay and straw agreed closely with that calculated from periods I and III in regard to all the constituents.

The seeds seem to be almost completely digested, and their addition has little effect on the digestibility of the hay and straw, except that a smaller percentage of the albuminoids of the straw appears to be assimilated in their presence.

The digestion of the albuminoids throughout the experiments shows

differences of from + 10·8 to − 4 per cent. from Stohman's expression $P' = \dfrac{P}{1 + \frac{1}{9}\dfrac{H + aC}{P}}$, when P = albuminoids in the consumed food; P′ = albuminoids digested; H = fibre; and aC = non-nitrogenous extractive matter + fat.

The mean of all the experiments is 2 6 per cent. in excess of the calculated quantity.

A table is given showing the ratio of the albuminoids to the non-nitrogenous extractive matter *plus* fat, and also the ratio in which these constituents were digested; it shows a close accordance between the digestibility of the nitrogenous and non-nitrogenous constituents, and that, as the proportion of albuminoids increased, a larger relative quantity was digested. Of water, sheep No. 1 took about double the weight of dry food consumed, and sheep No. 2 about 1½ times the weight of dry food; somewhat more was taken during the period of hay feeding.

E. K.

Spectroscopic Examination of the Chlorophyll in the Residues of Digestion. By J. Chautard (Compt. rend., lxxvi, 103—105).

The author has extracted the excrement of man, the horse, the cow, the sheep, the dog, the cat, the rabbit, and that of fowls, with alcohol, and examined the solutions spectroscopically for chlorophyll. It was found that the alcoholic extract absorbed the more refrangible rays of the spectrum forming the two dark bands in the red (between B and C of Fraünhofer) and orange which are so characteristic of chlorophyll. Thus, it would seem, that the chlorophyll had not undergone any other change than that which the lapse of time or the action of acids usually causes. The alcoholic tincture of cantharides also contains chlorophyll, which must be due to the presence of the *débris* of the leaves on which the insect feeds, as the extract of the elytra did not give the dark bands. Other insects gave similar results.

C. E. G.

Poisonous Properties of Calcium Salts.
By Rabuteau and L. Ducoudray (Compt. rend., lxxvi, 349—351).

The authors have experimented upon dogs by injecting aqueous solutions of calcium chloride into the veins. They find the action of this salt to resemble that of potassium chloride in nature and in intensity when quantities equivalent to equal weights of the metals are taken. The atomic weights of these metals are nearly the same, 39 and 40, and it is pointed out that Rabuteau in 1867 announced as a law that (comparable) metals are poisonous in proportion to their atomic weights or to the feebleness of their specific heats.

Death results from arrest of the heart's action, calcium being, like all other metals, except sodium and lithium, a muscle-poison. Muscles steeped in calcium chloride solution, lose their irritability sooner than

when steeped in pure water, but at first they contract more actively. This is in accordance with the fact that calcium chloride in a dose not too rapidly fatal causes a temporary acceleration of the heart's action before its retarding effect is produced.

E. D.

The Spontaneous Alteration of Eggs. By U. GAYON (Compt. rend., lxxvi, 232, 233).

THE author finds that the spontaneous decomposition occurring in eggs is invariably accompanied by the presence of microscopic organisms (vibriones); these are, he thinks, derived from the oviduct of the bird.

T. S.

Chemistry of Vegetable Physiology and Agriculture.

A Lecture Experiment in Vegetable Physiology. By W. WOLF (Chem. Centr., 1872, 722).

THAT it is essential to plant life that the roots should obtain oxygen, may be shown by transferring a plant grown by water-culture into water saturated with carbonic acid; the plant soon fades, but recovers when again placed in pure water.

R. W.

Influence of various Manures on Different Species of Plants. By M. T. MASTERS and J. H. GILBERT (Jour. Roy. Horticultural Soc., 1872, 19—80; and 1873, 124—158).

IN Mr. Lawes' experiments on meadow land, the action of manure in favouring certain species of plants is strikingly seen; with the view of elucidating this action, experiments were conducted for two years at Chiswick. Twelve meadow plants were grown separately in wooden boxes, both without manure, and with five manures; these consisted of a mixed cinereal manure (supplying phosphates, potash, &c), ammonium salts, sodium nitrate, cinereals and ammonia, and cinereals with sodium nitrate. The soil employed seems to have been too rich; the two seasons were also very different, and their results are to some extent contradictory.

Of the three clovers, *Trifolium pratense*, and *repens* were in the first season much benefited by the cinereal manure, while *Lotus corniculatus* seemed actually injured. In the second season, the cinereal manure alone had little effect on the clovers. In both seasons nitrogenous manures with cinereals gave the largest crops.

With the six grasses cinereal manure alone had little effect, save in the first season with *Lolium perenne*. *Dactylis glomerata* appeared to be specially benefited by ammonia, and *Anthoxanthum odoratum*, and perhaps *Bromus mollis*, by nitrates; but in almost every case the best crop was from a mixture of cinereals with nitrogen.

Of the miscellaneous species, *Carum Carui* was distinctly benefited by cinereal manure. *Carum Carui* and *Plantago lanceolata* reached their maximum with nitrates and cinereals, and *Achillea Millefolium*, with cinereals and ammonia.

In no case did the habit of growth of the plant appear altered by the influence of the manure. Observations on the development of the roots confirmed the opinion, that those plants which dispossess others under liberal manuring, are those whose habit of growth gives them the widest hold of the soil.

R. W.

Action of the Volcanic Earth of the Solfatara of Puzzuoli on Diseases of the Vine. By S. DE LUCA (Compt. rend., lxxvi, 359—360).

THIS earth contains sulphur in the form of crystals and small amorphous conglomerations, traces of sulphide of arsenic, and porous volcanic matters, formed for the most part of the silicates of decomposed trachytes. Reduced to fine powder, it produces the best results on the vine by the sulphuring process It also acts beneficially in several ways when placed round the vine stocks at a small depth below the surface, and possesses properties not belonging to sulphur alone.

E. D.

Effect of Manures on the Alkaloidal yield of Cinchonas. (Pharm. J. Trans. [3], iii, 521.)

FROM experiments made by Mr. Broughton, the Government Quinologist at the Ootacamund Plantation, in the Department of Madras, it appears that the use of artificial and natural manures increases the alkaloidal yield of the cinchonas. Some fine three-year-old plants of *Cinchona succirubra* were treated in November, 1869, in plots of fifty each, with 1 lb. of ammonium sulphate, and the same quantity of guano. No perceptible increase in luxuriance or rapidity of growth was perceived to result, but in January, 1872, the difference in the alkaloidal yield of bark from the manured and non-manured plants was as follows:—

	Manured.	Unmanured.
Total alkaloids	7·25	4·89 per cent.
Quinine	2·45	1·78 „
Cinchonidine and cinchonine ..	4·80	3·11 „

The stem-bark of trees manured with 1 lb. of guano, gave the following results, as against trees not so treated:—

	Manured.	Unmanured.
Total alkaloïds	5·29	4·76 per cent.
Quinine	0·91	1·04 „
Cinchonidine	4·38	3·72 „

The loss in quinine and small gain in total alkaloïds may possibly be

owing to the exciting action of the guano hastening the change through which, as this species grows older, it loses its alkaloïdal character. Mr. Broughton, therefore, does not recommend that *C. succirubra* should be manured, as the cost of manure would outweigh the small increased richness in the bark.

C. officinalis has always been noted for its extreme sensitiveness to situation, sunlight, and character of soil. Trees of this species, treated with 1 lb. of guano, although differing in no respect from unmanured trees while growing, yielded bark containing the following percentages of alkaloïds:—

	Manured.	Unmanured.
Total alkaloïds	6·51	3·98 per cent.
Pure quinine	4·41	2·40 „
Cinchonidine and cinchonine ..	2·10	1·58 „

Trees of the same species, treated with ¾ lb. ammonium sulphate, gave results as under:—

	Manured.	Unmanured.
Total alkaloïds	5·76	4·54 per cent.
Pure quinine	3·11	2·54 „
Cinchonidine and cinchonine ..	2·65	2·00 „

From 1867 to 1872 trees of this species were treated with about four barrow-loads of farmyard manure each. In February, 1872, bark from trees so manured, and from similar trees unmanured, gave the following results:—

	Manured.	Unmanured.
Total alkaloïds	7·49	4·68 per cent.
Pure quinine	7·15	2·40 „
Cinchonidine and cinchonine ..	0·34	2·28 „

Farmyard manure is therefore superior to artificial manure for this purpose, and favours the production of quinine over cinchonidine and cinchonine.

As no outward difference could be observed in the manured trees from those not so treated, Mr. Broughton is of opinion that the alkaloïds are not specially active constituents in the processes connected with the life and growth of the plant.

J. B.

On the Leaves of Cinchona Succirubra. By J. E. HOWARD (Pharm. J. Trans. [3], iii, 541).

FROM about 20 lbs. of dried leaves, the quantity of alkaloïd obtained was so small as to lead the author to believe that the leaves contain no alkaloïd whatever, and that the minute quantity found must have been due to the presence of fragments of bark of small branches, accidentally mingled with the leaves.

J. B.

Distribution of the Alkaloïds in Cinchona Barks.

By P. CARLES (Bull. Soc. Chim. [2], xix, 51—54).

THE author has made a considerable number of analyses of barks from different species of cinchona, with the view of ascertaining in which portion of the bark the alkaloids chiefly reside. The results of his experiments show that the outer cellular layers of the bark contain most of the quinine, and probably also the cinchonine. In one or two instances, however, he found a considerable proportion of cinchonine in the liber.

These experiments confirm the opinion of Howard on the same subject.

W. A. T.

Constituents of the Ash of various parts of the Coffee Tree.

By HERMANN LUDWIG (Arch. Pharm. [3], i, 482—494).

THE following table contains the results of the author's analyses of the ash of the undermentioned parts of the coffee tree, grown in Brazil:—

	I.	II.	III.	IV.	V.	VI.	VII.
K_2O	16 24	3·99	14 95	15 56	15 87	14·13	44·03
Na_2O	2·18	6·66	1·13	trace	5·10	5·84	5·85
CaO	27·04	38 04	20·82	16·83	21·92	8 64	4·89
MgO	4·15	5·39	7·96	5·63	4·62	8·14	8·01
Fe_2O_3	3·39	5·03	3·58	11·38	7·12	16·54	1·96
Mn_3O_4	0 44	trace	0 40	trace	—	trace	trace
Al_2O_3	7 85	1 59	9 11	trace	4 19	2·78	trace
SiO_2	6·16	1·23	9·60	15·16	9·25	1·65	0·37
CO_2	27·55	25 16	21·03	20·13	13·28	8·34	21·24
P_2O_5	2·28	11·30	6·23	9 99	16·70	18·65	10·54
SO_3	2 26	1·38	3·99	3·94	1·95	15·28	1·64
Cl	1·05	0·25	1·56	1·34	trace	trace	0·98
I	—	—	—	0·88	—	—	—
	100·59	100 02	100·36	100·84	100·00	99·99	99·51

I. Root of a young tree in bearing. II. Root of an old tree. III. Leaves. IV. Pulp of the pericarp. V. Parchment-like coating of coffee-beans. VI. Coffee-beans grown on gneiss soil. VII. Coffee-beans grown on limestone soil.

The amount of phosphoric acid in young trees increases from the root to the fruit and its separate parts. The increased proportion of this acid in the roots of old trees is remarkable.

From analyses of the ash of coffee-beans of various growths made by Graham, Stenhouse, and Campbell (*Qu. Journ. Chem. Soc.* ix, 33) these chemists inferred that sodium-compounds and silica are entirely wanting in that part of the tree. The inference is not borne out by the present analyses, which show the presence of considerable quantities of sodium. The silica found by the author in the ash of the beans may, he thinks, be derived from small quantities of adhering earth, but that silica is

an essential constituent of other parts of the tree is clearly shown by the fact that it increases in amount from the root to the leaves and pulp, decreases in the parchment-like coating of the beans, and suddenly disappears in the beans themselves.

Manganese has been overlooked by other analysts.

The influence of the soil upon the ash-constituents is shown in a marked manner in the amount of potash, iron, &c., in columns VI and VII.

J. R.

Analytical Chemistry.

Lecture Experiments with the Thermo-analyser.

By E. MULDER (Deut. Chem. Ges. Ber., v, 1078—1080).

THE thermo-analyser consists of a mercurial pneumatic trough in the bottom of which is a stuffing-box, in which slides an iron or copper tube closed at the upper extremity. With this arrangement, it is easy to make the closed end of the sliding metal tube pass upwards into a measured quantity of gas standing over the mercury. If it be now required to ignite the metal composing the sliding tube (copper or iron) in the gas, it is only necessary to pass an oxy-hydrogen blowpipe upwards through the open end of the sliding tube, and so to ignite the closed end which projects above the mercury and enters the gas to be acted on. When a gas is to be subjected to the action of an oxidising agent, such as copper oxide or potassium bichromate, a depression must be made in the closed end of the sliding tube, and the reagent must be placed in the cavity thus formed.

To demonstrate the composition of alcohol with this apparatus, the outer tube containing the substance is surrounded with steam so as to volatilise the alcohol. Cupric oxide is then ignited in the vapour, the products are measured, and after the water has been absorbed by calcium chloride, the volume of carbonic acid is read off.

In case this apparatus is used for experiments on dissociation, it may be necessary to make the sliding tube of platinum.

Mr. Wynkes is engaged in studying the application of the thermo-analyser to a variety of quantitative analyses.

T. B.

Siphon Apparatus for Filtration. By H. DAHLEN (Zeitschr. Anal. Chem., xi, 184—186).

THE description of this apparatus, a combination of an asbestos filter with a siphon arrangement, requires the diagrams accompanying it to render it intelligible.

E. D.

Washing Gelatinous Precipitates.

By J. M. Chautard (Zeitschr. Anal. Chem., xi, 299).

When a gelatinous precipitate is to be washed, much time may be saved by adding an excess of the precipitant, and evaporating the whole until a dry powder is obtained; this may then be readily washed on the filter. Thus 68·02 and 68·13 per cent. of chromic oxide were obtained from potassium dichromate, the calculated amount being 68·04; 10·89 and 10·88 per cent. of alumina were found in potash alum, the calculated percentage being 10·86; and 14·28 and 14·29 of ferric oxide from ferrous ammonium sulphate instead of 14·29.

C. R. A. W.

Estimation of Chlorine, Bromine, and Iodine by Carius' Method. By E. Linnemann (Zeitschr. Anal. Chem., xi, 325).

Iodide of silver is partially soluble in nitric acid and in solution of silver nitrate. The best results are obtained by taking 0·5 to 0·8 gram of iodide, $1\frac{1}{2}$ equivalents silver nitrate, 2 c.c. water, and 2 c.c. nitric acid of specific gravity 1·29. The silver nitrate is dissolved in the water in the tube, and the nitric acid added, whereby much of the nitrate is precipitated in fine crystals; the heating is continued for three hours at 180°—200° C.; the contents of the tube are diluted with 200 c.c. of lukewarm water, and boiled ten minutes. Even with these precautions the percentage of iodine is frequently found to be 0·6 to 1·0 per cent. too small; with bromine and chlorine, the errors are much less.

Note by Abstractor.—The abstractor can corroborate the statement that a smaller percentage of iodine is obtained if silver iodide be precipitated in a solution containing much silver nitrate and nitric acid, a higher percentage being obtainable by greatly diluting such a liquid.

C. R. A. W.

Ferric Chloride as a Test for Iodine. By Tessier (Zeitschr. Anal. Chem., xi, 313).

In presence of tannin, iodine cannot be recognised by the ordinary reagents, but is immediately separated by the addition of a few drops of neutral ferric chloride solution at a temperature of 30° R. (37·5° C.), and can then be recognised by the starch reaction.

C. R. A. W.

Recognition of the Presence of Potassium Bromide in Potassium Iodide. By E. van Melckebeke (Chem. Centr., 1872, 586).

Ten c.c. of a saturated solution of potassium bromide are diluted with 10 parts of distilled water, and 1 grm. of the coarsely powdered potas-

sium iodide is added with agitation. If the potassium iodide dissolves immediately, it may be considered free from bromide. If it contains potassium bromide, this latter will remain undissolved for some time.

When the potassium iodide is added to the potassium bromide solution slowly and in small portions at a time, it is not necessary to dilute the solution with water.

T. B.

Testing of Potassium Bromide for Iodine and Chlorine. By H. Hager (Chem. Centr., 1872, 617).

To test potassium bromide for iodine, 0·1 grm. of the sample is dissolved in 10—12 c.c. of 10 per cent. ammonia-solution, and a drop of silver nitrate solution is added. A turbidity, which does not disappear on agitation, indicates the presence of iodine.

To test for chlorine, 0·1 grm. of the sample is dissolved in 3—4 c.c. of water and precipitated with 0·26 grm. of silver nitrate dissolved in the same quantity of water. The precipitate thus produced is washed with water, and then treated with a mixture of 3 c.c. of water and 3 c.c. of the officinal ammonia carbonate solution of the *Pharmacopœia Germanica;* * the ammoniacal solution is now filtered and neutralised with nitric acid. A slight opalescence, which does not interfere with the transparency of the liquid, indicates that the sample is free from chlorine; a considerable turbidity or a precipitate indicates that chlorine is present.

T. B.

Estimation of Bromide in Iodide of Potassium. By J. Lepage (Chem. Centr., 1872, 537).

The iodide is supposed to be free from mercurous chloride, and from carbonate and iodate. 1 gram is dissolved in 30 grams of water, and to this there is added, from a burette, a solution of 1 gram mercuric chloride in 20 c.c of water, as long as a milkiness is produced.

If the potassium iodide is pure, at least 16 c.c. of the mercuric chloride solution will be required for this purpose; in the contrary case, a portion of the latter will remain over, greater in proportion to the quantity of bromide in the iodide.

Mercuric bromide, being soluble, is not precipitated.

To detect the bromine in the supernatant liquid, the precipitate, after settling, is removed by filtration, and the filtrate is evaporated to 20 c.c., cooled and boiled with a drop of ferric chloride solution so long as iodine vapours are evolved. The liquid is then filtered, chlorine water added, and bromine recognised by the usual tests.

M. M. P. M.

Arsenical Hydrofluoric Acid. By Carl Jehn (Arch. Pharm. [3], i, 481).

Commercial hydrofluoric acid generally contains arsenic as trioxide. When this acid is used to dissolve silicates containing ferrous and ferric

* This solution, like that of the P. L., is made by dissolving 1 part of the salt in 5 parts of water.

oxides, and the ferrous oxide is afterwards estimated by titration with permanganate, errors may arise from the circumstance that arsenic trioxide is oxidised by permanganate. Such errors may be avoided by previously oxidising the arsenic, if present, by means of permanganate.

J. R.

Volumetric Estimation of Sulphuric Acid. By E. FLEISCHER (Zeitschr. Anal. Chem. xi, 309).

WILDENSTEIN'S method (addition of a known quantity of barium chloride and estimation of the excess by neutual chromate of potassium solution) is applicable to substances other than the salts of the alkali metals; if the liquid is acid, ammonia solution (free from carbonate) must be added; or as the presence of traces of carbonate is almost unavoidable, a couple of drops of calcium chloride or acetate should be added to the ammoniacal liquid, and the whole boiled.

Magnesium, zinc, and cadmium sulphates can be readily examined thus; but nickel, cobalt, and copper salts yield coloured solutions, and hence prevent the terminal reaction (production of a yellow liquid) from being seen. An ammoniacal solution of lead acetate may be used as an indicator, as a yellow-red precipitate is formed by a very minute amount of chromic acid.

C. R. A. W.

Estimation of Nitric Acid. By F. SCHULZE (Zeitschr. Anal. Chem., xi, 313).

THE concentrated water, &c., is boiled in a vessel furnished with a gas delivery tube, which is closed by a caoutchouc valve when the air is expelled; a partial vacuum being formed on cooling, some hydrochloric acid and ferrous chloride solution are sucked up. Nitric oxide is thus produced, and is led off into a measuring apparatus, the last portion being expelled by boiling, and the nitric oxide being estimated by absorption with ferrous chloride solution. Organic matters in the water exert no injurious influence, and the traces of hydrochloric acid gas expelled are too small to be appreciable.

Wagner estimates nitric acid by fusing the substance with oxide of chromium and sodium carbonate; the estimation is effected either by determining the chromic acid formed, or the nitric oxide evolved, the latter being estimated by adding oxygen and absorbing the nitrous acid by normal soda-solution, the excess of soda being determined by a standard acid solution. This method is applicable to potable waters if the organic matter be previously oxidised with pure permanganate of potassium in a solution containing sodium carbonate; sulphuric acid is then added in sufficient excess to destroy any oxalic acid that may have been formed, then baryta-water till the liquid is alkaline; finally, the whole is evaporated to dryness with addition of sodium carbonate, mixed with chromic oxide and sodium carbonate, and transferred to a tube furnished with a gas-delivery pipe and containing some sodium bicarbonate at the end. The evolved nitric oxide is received in a vessel containing oxygen and the known bulk of diluted soda-solution, and standing over mercury.

Commercial Analysis of Nitrates. By H. Joule (Compt. rend., lxxvi, 230).

The method commonly adopted for the commercial analysis of nitrates, consists in estimating separately the percentage of foreign matter (water, chlorides, sulphates, &c.) and calculating the nitrate, and consequently the available nitric acid, by difference. This plan introduces serious errors, more especially when a mixture of potassium and sodium nitrates is operated on.

The author's improvement is as follows:—The nitrate is converted directly into chloride by ignition in a crucible with sal-ammoniac, and the chlorine is estimated before and after the operation by means of a standard solution of silver nitrate. The difference between the two results gives the chlorine which has replaced the nitric acid, and the proportion of the latter contained in the sample is calculated by multiplying the number found by the factor, 1·52. With practice it is easy to ascertain by the weight of the crucible before and after ignition, whether the nitrate is comparatively pure, or whether it contains much foreign matter. In the latter case, it is sometimes advisable to make a direct estimation of the foreign matter.

J. W.

Superphosphates, their Adulterations and Valuation. By J. E. Reynolds (Chem. News, xxvi, 291—293).

For the valuation of superphosphates, the author employs a series of numbers inversely proportional to the relative commercial values of the constituents of the manure. These numbers, referred to ammonia as unity, are:—Ammonia, 1·0; latent ammonia, 2·2; biphosphate of lime, 4·0; bone phosphate, 8·0; mineral phosphate, 13·0; alkaline salts, 22·5. They indicate the replacing values of the different bodies to the manufacturer. The parts of these constituents in 10,000 of the manure are divided by the corresponding equivalent in the above series, and the several quotients added together; from the sum obtained (called degrees on the Royal Dublin Society scale) the value of the superphosphate is estimated by reference to a standard, which is fixed at 620° for a mineral superphosphate costing £6 10*s.*; or, as can be deduced from this, and is also obtained by comparison with analyses of bone superphosphates, 763° for a bone superphosphate costing £8.

E. K.

Estimation of Sulphur in Pyrites. By P. Holland (Chem. News, xxvii, 15).

The author obtained good results by fusing one gram of pyrites in an exceedingly fine powder, with nine or ten grams of a mixture consisting of equal parts of nitre and sodium carbonate (obtained by igniting the acid carbonate); and subsequently titrating the mixture with baryta-water.

J. B.

On a Source of Error in the Valuation of Pyrites.
By N. GLENDINNING and A. J. M. EDGER (Chem. News, xxvii, 13).

THE use of a Wedgwood or porcelain mortar for pounding pyrites prior to the estimation of sulphur, is one of the principal causes of the discordant results so frequently obtained by different chemists. By the disintegration of such mortars during the pounding, the percentage of sand is found too high, and the sulphur too low. In experiments upon the same sample of pyrites, it has been found that with steel or agate mortars the percentage of sulphur was from 1·24 to 2·80 higher, and the percentage of sand from 2·68 to 5·39 lower than when Wedgwood or porcelain mortars were used.

J. B.

Estimation of Small Quantities of Manganese.
By T. M. CHATARD (Zeitschr. Anal. Chem., xi, 308).

THE manganese compound is boiled with nitric acid and peroxide of lead; and the permanganate thus produced is titrated with a solution of oxalate of ammonium, of which 1 c.c. represents 0·0005467 manganese. Only small quantities of manganese can be thus estimated, inasmuch as the conversion into permanganate is incomplete if larger amounts be employed.

C. R. A. W.

New Reaction for Bismuth.
By v. KOBELL (Zeitschr. Anal. Chem., xi, 311).

A MIXTURE of potassium iodide and flowers of sulphur in equal proportions is added, and the whole heated on charcoal before the blowpipe; the production of bright scarlet very volatile bismuth iodide ensues, even when only traces of the metal are present.

C. R. A. W.

Titration of Ferrous Chloride with Potassium Permanganate.
By O. FOLLENIUS (Zeitschr. Anal. Chem., xi, 177).

THE author finds that Finkener's statement (Rose, ii, 926, 6th edition) that the injurious effect of hydrochloric acid in the titration of iron by permanganate is entirely prevented by the addition of hydrofluoric acid and potassium sulphate, is without foundation. This addition is without effect on the result of the titration.

E. D.

Quantitative Determination of Uranium.
By O. FOLLENIUS (Zeitschr. Anal. Chem., xi, 179—181).

THE author shows, by a series of titrations of uranous salts with potassium permanganate, firstly, that hydrochloric acid exerts the same injurious action that it does in the estimation of ferrous salts; and, secondly, that the error arising from its presence may be avoided in the same way as in the case of ferrous salts, namely, by the successive

addition and reduction of the uranous solution until the proportion of permanganate required becomes constant.

E. D.

Determination of Nitrogen in Organic Substances. By MÄRKER (Chem. Centr., 1872, 726).

WHEN highly nitrogenous bodies, as glutin or muscle, are burnt in the ordinary way with soda-lime, the amount of nitrogen found is too low if the determination be made by the titration method; but if precipitation by platinum be employed, the results are exact, and agree with determinations by Dumas' method.

R. W.

A New Method of Testing the Inflammability of Petroleum and other Hydrocarbons. By VAN DER WEYDE (Zeitschr. Anal. Chem., xi, 338).

A GRADUATED glass tube closed at one end is filled with the oil to be tested and inverted in a vessel of water, which is kept at 43·3°—44° The comparative inflammability of the oil is estimated by the volume of vapour which collects in the tube. A very crude method.

J. R.

A New Method of Testing Alcohol for Fousel Oil. By BOUVIER (Zeitschr. Anal. Chem., xi, 343).

A few pieces of potassium iodide are added to the alcohol in a test-tube, which is shaken gently. If the alcohol contains 0·5 or 1 per cent. of fousel oil, a distinct yellow colour appears in a few minutes; the reaction is visible even with ·2 per cent. of the oil.

Böttger, whose experiments confirm this statement, finds that the coloration is due, not to amyl alcohol itself, but to an acid which accompanies it and decomposes the potassium iodide.

J. R.

A Simple Process for the Detection of Water and Alcohol in Ether. By R. BÖTTGER (Chem. Centr. 1872, 742).

ETHER, when quite free from water, will mix with an equal volume of carbon sulphide, forming a perfectly clear solution; but if the smallest quantity of water is present, the liquid appears milky. If the sample shaken up with a small piece of potassium hydrate assumes, in the course of 24 hours, a yellowish colour, alcohol is present.

W. A. T.

Estimation of Alcohol in Volatile Oils. By R. BÖTTGER (Chem. Centr., 1872, 742).

THIS process is based on the fact that anhydrous glycerin is not miscible with volatile oils, but is easily soluble in alcohol. By shaking up in a graduated tube pure glycerin with an equal volume of the oil to

be tested, and allowing the liquids to separate, the increase in the volume of the glycerin indicates the amount of alcohol present in the sample.

W. A. T.

A Simple Method for the Quantitative Estimation of Alcohol in the Chloroform of Commerce. By A. C. Oudemans, Junr. (Ann. Chem. Pharm., clxvi, 78).

In another paper the author has shown that cinchonine is much less soluble in pure chloroform than in a mixture of much chloroform and little alcohol. The process he recommends for the estimation of alcohol in chloroform is founded on this fact. He employs cinchonine which has been precipitated from one by its salts by ammonia.

The following table contains the results of actual experiments:—

Percentage by weight of alcohol, C_2H_6O.	Residue left by 5 c.c. of the chloroform solution of cinchonine measured at 17° C.	Difference.
0	21 milligrams.	—
1	67 ,,	46
2	111 ,,	44
3	152 ,,	41
4	190 ,,	38
5	226 ,,	36
6	260 ,,	34
7	290 ,,	30
8	318 ,,	28
9	343 ,,	25
10	366 ,,	23

W. A. T.

New Reaction of Phenol. By P. C. Plugge (Zeitschr. Anal. Chem., xi, 173).

Phenol solutions boiled with a solution of mercurous nitrate, besides slowly reducing the mercury and evolving an odour of salicylol, impart a deep red colour to the solution. The production of the colour is due to the presence of traces of nitrous acid; much more than a trace of this acid renders the colour indistinct. The reaction is very distinct with $\frac{1}{60,000}$ of phenol, and is still apparent when only $\frac{1}{200,000}$ is present.

Salicylol and salicylic acid, as well as the products of the distillation of tyrosine (which, according to Städeler, contain phenol), behave like phenol.

Benzene is coloured bright yellow; aniline in not too small quantity, a deep yellow. Benzoic acid, hippuric acid, salicin, and helicin are not coloured.

Tyrosine assumes a light red, and after longer boiling a yellow colour. The red colour is relatively much weaker than that caused by Hoffmann's reagent and is yellowish, while the latter is purplish. Hoffmann's reagent gives a red colour with phenol, but of a somewhat different tint from that produced by the mercurous solution, and rela-

tively much weaker. The author's phenol-reaction cannot therefore be confounded with Hoffmann's tyrosine-reaction.

E. D.

Lex's Test for Phenol with Ammonia and Bleaching Powder. By E. SALKOWSKI (Zeitschr. Anal. Chem., xi, 316).

THE liquid to be examined is mixed with one-fourth its volume of ammonia, and a few drops of bleaching-powder solution (1 to 20 of water), and then warmed but not heated to boiling; a blue coloration (green in very dilute liquids), becoming red on addition of sulphuric or hydrochloric acid is produced if phenol be present. Solutions containing $\frac{1}{4000}$ part of phenol give a strong blue reaction, while ferric chloride gives no colour with a solution containing $\frac{1}{2000}$.

C. R. A. W.

Detection of Grape- and Milk-sugar. By G. CAMPANI (Zeitschr. Anal. Chem., xi, 321).

GLUCOSE can be detected in diabetic urine by the addition of 5 c.c. of a mixture of concentrated solution of lead acetate and dilute solution of crystallised copper acetate; the liquid being heated to boiling, a yellow tint is produced if a trace of glucose be present, and on standing a yellow precipitate appears. With larger quantities of glucose an orange-red precipitate is formed.

Cane-sugar is unaffected by this reagent; milk-sugar gives a yellow tint in dilute solutions, red in concentrated ones.

Traces of copper may be conveniently detected by the addition of glucose and lead acetate, and boiling.

C. R. A. W.

Discrimination of Gum Arabic and Dextrin. By H. HAGER (Zeitschr. Anal. Chem., xi, 350).

GUM contains no dextroglucose, which, however, is present in dextrin, and may be found by Trommsdorff's sugar-test.

Gum contains a lime-compound: hence its solution is rendered turbid and milky by oxalic acid, whilst a solution of dextrin remains almost clear.

Gum gives a slimy yellow deposit when its solution is mixed with a neutral ferric salt.

J. R.

Determination of Cellulose. By KÖNIG (Chem. Centr., 1872, 728).

WORKING with rye-straw and clover hay, the author finds that the finer the state of division of the material, the smaller is the quantity of cellulose obtained; a uniform preparation of samples is thus essential.

R. W.

Detection of Morphine in Quinine. By H. Hager (Chem. Centr., 1872, 727).

In suspected cases add a little of the salt to a solution of potassium ferricyanide, to which some ferric chloride and a little hydrochloric acid have been added; if morphine (or any other deoxidising substance) be present, the solution speedily becomes blue.

R. W.

Use of Chloroform in Forensic Chemistry. By J. Nowak (Chem. Centr., 1872, 536).

By shaking up alkaline solutions of strychnine, quinine, quinidine, cinchonine, caffeine, theobromine, emetine, atropine, hyoscyamine, aconitine, veratrine, physostigmine, narcotine, codeine, thebaine, nicotine, or coniine with chloroform, these alkaloïds are dissolved in the chloroform, even in the cold. Brucine, colchicine and papaverine are also dissolved after some time. Sabadilline and narceine (the latter partially) are dissolved on the application of heat. Picrotoxine is easily dissolved from acid solutions. Morphine and solanine are insoluble in chloroform. By agitating the chloroform solution of any of the above alkaloïds with acidified water, the alkaloïd is taken up by the acid, and may thus be easily obtained in a very pure state.

M. M. P. M.

Estimation of Uric Acid by Bunsen's Process. By O. Schultzen and M. Nencki (Zeitschr. Anal. Chem. xi, 326).

A known weight, A, of urine is mixed with a weight, B, of solution of ammoniacal barium chloride, and the whole filtered into a flask the lip of which has been greased; the flask and its contents are weighed, and the contents transferred to a glass tube, which is then sealed up and heated to 200° for five or six hours. The barium precipitate is washed and weighed, its weight being b; the barium carbonate formed by the decomposition of the uric acid is weighed, its weight being K (the portion adhering to the tube being dissolved off by hydrochloric acid, converted into sulphate, and reckoned as carbonate). If C be the weight of urine mixture actually contained in the sealed tube (excluding the washings of the filter), the percentage of uric acid is given by the formula—

$$P = \frac{30{\cdot}41\ K(A + B - b)}{A\ .\ C\ .}.$$

Treskin finds that this process is also available for the estimation of uric acid in blood; the blood is precipitated by addition of alcohol, the precipitate washed out with alcohol, and the filtrate evaporated to dryness. The residue is exhausted with alcohol, and the filtrate evaporated and dissolved in water; the solution is precipitated with lead acetate, the excess of lead removed by ammonium sulphide, and the filtrate treated by Bunsen's process.

Creatinine gives off about half its carbon as carbon dioxide by this mode of treatment; and Hoppe-Seyler has shown that sugar, starch,

and cellulose also are decomposed, with evolution of carbon dioxide, on heating with alkaline solutions.

C. R. A. W.

Estimation of Uric Acid in Diabetic Urine. By E. KULZ (Zeitschr. Anal. Chem., xi, 357—358).

THE author has successfully employed the process of Naunyn and Riess, with some slight modifications in details. The paper does not admit of useful abstraction.

J. R.

Estimation of Sulphur and of Taurocholic and Glycocholic Acids in Bile. By E. KULZ (Zeitschr. Anal. Chem., xi, 353—354).

FOR the estimation of sulphur, the author adopts the method of Carius, which consists in oxidising the bile by heating it with nitric acid in sealed tubes, &c. He recommends, however, the use of dried bile, having found in his experiments with liquid bile that the percentage error is very considerable (5—10 p.c.), which result he attributes, not to defects in the method, but to the circumstance that very small quantities of bile were employed, and that bile contains only a small proportion of solid constituents (ox-bile, 6—8 p.c). The bile is best dried in successive thin layers in a porcelain boat, which is afterwards introduced into a glass tube with nitric acid. The solid constituents of the bile may, of course, be estimated at the same time.

For the estimation of taurocholic and glycocholic acids, the author first determines the total alkali-salts of bile-acids by Hoppe's process. He then determines the sulphur in a small portion of these salts by Carius's method. From the sulphur the amount of taurocholic acid may be calculated, and the glycocholic acid is found by difference.

J. R.

Indications of a Nitrite in Saliva. By R. BÖTTGER (Chem. Centr., 1872, 741).

ACCORDING to the author, the blue reaction is produced when saliva is acidified with sulphuric acid and a mixture of cadmium iodide and starch added.

W. A. T.

Detection of Sulphocyanogen in Saliva. By R. BÖTTGER (Zeitschr. Anal. Chem., xi, 350).

THE author recommends, in preference to the usual test (ferric salt), a strip of Swedish filter-paper impregnated with tincture of guaiacum, dried, and afterwards passed through a solution of copper sulphate (1 in 2000). Paper thus prepared instantly turns blue when moistened with saliva.

J. R.

Analysis of Milk for Clinical Purposes. By JOHN MUTER (Zeitschr. Anal. Chem., xi, 350—351).

AN application of Frankland's method of water-analysis to the examination of human milk. Five drops of the milk to be analysed are dropped upon a weighed quantity of dry copper oxide contained in a small paper filter; weighed; dried at 105°, to determine water and solid residue; then burnt with more copper oxide in an exhausted combustion tube. The gases of combustion are collected by means of a Sprengel pump, and analysed in the usual manner.

The author gives the following example:—

Milk taken.	Solid residue.	Nitrogen.	Carbon.
0·24	0·0264	00014	0·0167
	=11·00 p.c.	=0·5833 p.c.	=6·958 p.c.

Hence, by calculation, the milk contained—

Water.	Protein substances.	Sugar and Fat.		
89·00	3·71	7·29	=	100

J. R.

Milk Testing. By J. GARSIDE (Pharm. J. Trans. [3], iii, 582).

A SMALL variation in temperature causes a great difference in the yield of cream. In each of the following experiments two graduated tubes were filled with milk from the same pail, and a uniform temperature was maintained for the time mentioned.

No.	Hours.	Temp. F.	Apparent percentage of cream.
1........	4	43°	14
		55°	$8\frac{1}{2}$
2........	4	45°	12
		60°	8
3........	2	45°	14
		60°	12

In other experiments no increase in the quantity of cream was perceived after three or four hours. J. B.

Pyrology or Fire-Analysis. By Capt. W. A. ROSS (Proc. Roy. Soc., xx, 448).

Technical Chemistry.

New Application of the Reduction of Silver Salts to the Reproduction of Designs. By M. RENAULT (Compt. rend., lxxx, 1766).

IT is well known that the oxygen-salts of silver impregnating paper or other organic material are easily reduced by copper, hydrogen, or

vapour of phosphorus, and that this is not the case with the haloïd salts of that metal.

The author of the present paper has applied these facts to the reproduction of engravings, drawings, and designs of that kind.

The sheet of paper on which the drawing is made is placed on the top of a sheet of cardboard which has previously been exposed to vapour of hydrochloric acid, and on the top of the drawing is spread a sheet of paper sensitized with an oxygen-salt of silver. The double nitrate of iron and silver is one of the best for this purpose. The vapours of the hydrochloric acid rising from the pasteboard beneath pass through the paper at all points, except those at which the lines of the picture are found. The oxy-salt in the sensitized paper quickly becomes converted into chloride of silver; but those points at which the hydrochloric acid has not penetrated remain in their old condition. When the paper thus treated is laid on a plate of copper, or exposed to hydrogen or vapour of phosphorus, the unchloridized parts blacken, and a perfect copy of the design is obtained, which may afterwards be fixed in the regular way. J. T. B.

The Chemistry of Sulphuric Acid Manufacture.

By H. A. Smith (Phil. Mag. [4], xlv, 23—40; and xlvi, 121—128).

The subjects treated of in this paper are:—1stly. An experimental examination of the causes which determine the mutual action of the gases in the lead chamber. 2ndly. The distribution of the gases in the lead chamber; and following from this, an inquiry into the best form of chamber to be used in the manufacture of sulphuric acid.

1stly. It is generally understood that no action takes place between *dry* sulphurous acid and nitric acid* gases when brought together in the same vessel, and in all chemical treatises this fact is distinctly stated. The presence of water has been regarded as indispensable to the mutual action resulting in the formation of sulphuric acid. The author, however, finds that "action does take place between the dry gases under certain conditions."

When dry sulphurous and nitric acid gases were brought into contact in a dry glass bulb, which was then hermetically sealed, there was apparently no action; but when this bulb, after being allowed to stand 10 or 12 days, was opened, and the remaining gases expelled, it was found that a decided though small quantity of sulphuric acid [anhydride] had been deposited on the sides of the vessel, and was observed in small, white, needle-shaped crystals, soluble in water, and behaving in all respects like sulphuric acid. The addition of a single drop of water on the end of a fine platinum wire, was found greatly to accelerate the action. The crystals were not identical with the ordinary chamber crystals, differing in form, and in the fact that they remained permanent for some time in the air, and in contact with water rapidly dissolved without liberation of nitrous fumes.

The same effect ensues, if the vessel with the dry gases be surrounded by ice, but a much longer time is required than when water is present. Sudden application of heat is likewise attended with similar results.

* What does the author mean by "dry nitric acid?" He says that it was prepared "from nitrate of soda by the action of sulphuric acid."—(Ed.)

It has been shown that a very small quantity of water will cause the action to commence at once; the effect of water present in large quantity upon the formation of acid was next tried.

1. A mixture of 2 vols. of steam to 1 of mixed gases was allowed to stand for 24 hours, the gases being mixed in the requisite proportion.

2. Another mixture of the same amount of mixed gases was passed into a similar vessel, but no air was allowed to enter, and the water was presented to the gases in the liquid state on a platinum wire, and the whole allowed to stand the same length of time as No. 1.

3. Equal volumes of steam and mixed gases were next tried.

The results were as follows:—

No. 1. 66 per cent. of acid produced.
No. 2. 93 „ „

A certain amount of nitric acid still remained untouched. In both cases the result was apparently a complete combination, but on examination a large amount of nitric acid was found in solution in water in No. 1.

No. 3. 74 per cent. of acid produced.

The volume of steam introduced should evidently be less than the combined volumes of the two gases.

The above experiments were now repeated, but the temperature of the vessels was raised to 100°. The results were as follows:—

No. 1. 86·7 per cent. of acid produced.
No. 2. 24·5 „ „
No. 3. 80·2 „ „

The following rule is deduced from the influence of rise of temperature, as shown in these and many other experiments:—"The higher the temperature the more steam is required." The next question to be answered was, "In what part of the vessel does most action take place?" A layer of concentrated sulphuric acid (previously weighed) was placed on the bottom of the vessel, and the gases were allowed to enter, steam being excluded. The gas at the upper part of the vessel became almost immediately nearly white, but a strong and long continued action seemed to be taking place close to the surface of the sulphuric acid, no apparent action being noticed towards the upper part of the vessel. On examination no sulphurous acid was found, whilst the weight of acid originally present was greatly increased. The vessel had stood for 24 hours. Owing to the unwieldiness of the apparatus, this process and plan could not be successfully reproduced on the large scale.

The subject of the next investigation was "The Distribution of Gases in the Lead Chamber, involving the question as to the best form of chamber to use."

The result of this investigation, in which samples of chamber gas were taken and analysed at every 10 feet along the length, 15 feet from the bottom, and also at the same distances 3 feet from the bottom, was that the greatest amount of condensation takes place at the bottom of the chamber, near the surface of any sulphuric acid that has been already formed, and that the upper portion of the chamber is merely of

use as a reservoir for the gases. A long low chamber was found to answer the same purpose, and to a greater degree than a long high one, and expense in chamber building may thus be greatly reduced.

In the conclusion of his paper, the author urges upon all sulphuric acid manufacturers to have a table drawn up to show the foreman of the chambers the amount of steam to throw in at every increase or diminution of temperature.

The author further shows by laboratory experiment that 200° F. is the point at which the mutual reaction between nitric and sulphurous acids takes place, and that the action is accompanied by a rise of temperature. In a series of experiments made in the sulphuric acid chambers themselves, it was found that in the zone of greatest action, viz., about 3 feet from the floor, and at about the centre of the chamber, the temperature of 200° F. was very nearly attained, and at 8 feet above the floor and higher, the maximum temperature attained gradually decreases, in proportion to the height from the floor.

It is stated that whenever the colour of the liquor from the Gay-Lussac Tower is a dark red, this is a sign of the escape either of nitric acid or some of the higher nitrogen oxides. The conclusions drawn and summed up are as follows:—

1. The best form of chamber to be employed is one which is long and not high, the results of experiment pointing to one somewhat of the following dimensions:—150 feet long, 25 to 30 feet wide, and about 10 to 12 feet high.

2. The temperature of the chamber to be kept as nearly as possible about 200° F., this also acting as a regulator for the amount of steam thrown in.

3. Sulphuric acid to be used instead of water on the chamber floor in starting.

W. S.

Glauber's Salts in Soda used for Making Glass. By H. E. Benrath (Chem. Centr., 1872, 528).—The object of this paper is to point out that very generally the soda used in the glass manufacture contains sulphate, and that when this is so a poor glass is produced. The addition of ·75—1 part of wood charcoal for every 100 parts of true soda improves the quality of the glass.

M. M. P. M.

Gas Apparatus for Heating in Laboratories. By Thomas Fletcher (Mechanics' Magazine, 1872, 253; Chem. Centr., 1872, 563).

Use of Water-glass in Building. By H. Wagner (Chem. Centr., 1872, 558).

Investigations on the Bessemer Process. By F. Kessler (Dingl. polyt. J., ccv, 436; Chem. Centr., 1872, 693).

Working of Titaniferous Iron Ores. By F. Wemmer (Chem. Centr., 1872, 823).

Gun-cotton and Collodion Preparations. By C. H. Mitchel (Amer. J. Pharm. [4], ii, 241; Chem. Centr., 1872, 554).

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXI.—*On a Method of Estimating Nitric, Chloric, and Iodic Acids.*

By T. E. THORPE, F.R.S.E.

1. OF the many processes which have been proposed for the estimation of nitric acid, those which depend upon its conversion into ammonia by nascent hydrogen, are on the whole the least liable to objection in point of principle. The means which we already possess of determining ammonia, whether in large or in small quantities, are expeditious and accurate. Starting from this principle, Schulze appears to have been the first to devise a method of estimating nitric acid capable of affording accurate results. The subsequent processes of Harcourt, of Siewert, and of Chapman, based upon the influence exerted by nascent hydrogen generated by the action of a strong solution of potash upon mixtures of iron and zinc or upon aluminium alone, are well known and are often used.

2. The principle of the method which forms the subject of the present communication, is identical with those in so far as it depends upon the conversion of the nitric acid into ammonia, but the manner of generating the hydrogen is entirely dissimilar. The new method is based upon a remarkable reaction recently described by Messrs. Gladstone and Tribe in the Proceedings of the Royal Society (vol. xx, p. 218). Some zinc-foil was allowed to remain in a solution of copper sulphate until its surface was covered with spongy copper. The metals were washed with distilled water and placed in a bottle of pure water. Small quantities of hydrogen were quickly evolved, the amount of which rapidly increased on gently heating the liquid. It was distinctly noticed that the hydrogen was evolved from the copper, and that zinc hydrate was simultaneously formed.

I have found that if a small quantity of nitre be added to the pure water surrounding the two metals, and the liquid be gently heated, not a trace of hydrogen will be evolved, but a distinct smell of ammonia will be perceived. A slip of turmeric paper placed in the flask over the heated liquid is turned brown, and if on boiling, the steam be led into water containing a few drops of reddened litmus solution, the colour will be changed to blue, and the water in the flask will acquire a permanent alkaline reaction from the formation of potassium hydroxide. The following experimental results show that the conversion of the nitric acid into ammonia is complete:

I. 40 grms. of thin sheet zinc were placed in a flask and coated with a bulky precipitate of copper by the action of a tolerably concentrated solution of copper sulphate for 10 or 15 minutes The metals were repeatedly washed by decantation with distilled water, care being taken to remove as little of the adherent copper as possible. The weighed quantity of potassium nitrate was then added, together with about 40 c.c. of water, and the flask was fitted with a caoutchouc stopper and bent tube connected with a three bulbed U-tube containing a small quantity of dilute hydrochloric acid. The liquid in the flask was gently boiled for 1 hour, and the contents of the U-tube were rinsed out into an evaporating basin, mixed with platinum tetrachloride and evaporated to dryness.

0·5090 grm. KNO_3 gave 1·0498 gram $PtCl_4.2NH_4Cl$ and
0·0301 gram metallic platinum.
Equivalent to 0·50908 grm. KNO_3.

II. The liquid in the flask was poured away, a small quantity of dilute hydrochloric acid was added, and the well washed residue was again covered with a solution of copper sulphate. After removing the sulphates by washing, a second quantity of nitre was weighed out into the flask and the above process was repeated.

0·4183 grm. KNO_3 gave 0·9208 gram $PtCl_4.2NH_4Cl$ and
0·0013 gram metallic platinum.
Equivalent to 0·4188 gram KNO_3.

III. A dilute solution of nitre was prepared by dissolving 0·9478 gram of pure nitre in water and diluting to 500 c.c. 25 c.c. of this solution, containing 0·04739 gram KNO_3, were used in all the following experiments. From 5 to 13 grams of sheet zinc were employed: the solution was occasionally gently heated for some time and then rapidly boiled for 15 or 20 minutes; sometimes, however, the liquid was heated directly to the boiling point and maintained in brisk ebullition for about an hour. The volume of the liquid in the flask was in general about 50 c.c., *i.e.* 25 c.c. of water were added to an equal bulk of the nitre solution. The ammonia was estimated as platinum-ammonium chloride. The following are some of the numbers obtained:—

KNO_3 used.	KNO_3 found.
0·0474 gram.	(1.) 0·0476 gram.
—	(2.) 0·0473 „
—	(3.) 0·0487 „
—	(4.) 0·0469 „

3. As the following experiments show, the presence of alkaline chlorides and sulphates is without influence upon the result.

1·0345 gram of nitre was dissolved in water, and the solution was diluted to 500 c.c. 25 c.c. of this solution would contain 0·05172 gram KNO_3. This amount of the liquid was used in all the following experiments:—

2·122 gram of common salt and 2·322 gram of potassium sulphate were dissolved in water, and the solution was diluted to 100 c.c. 5 c.c. of the solution of the mixed salts would contain 0·1061 gram NaCl and 0·1162 gram K_2SO_4. This quantity of the solution was mixed with the nitre in all the following determinations. The conditions of experiment were in other respects similar to those in the foregoing series. The same sheet zinc was used repeatedly after washing with dilute hydrochloric acid and water. The copper solution was always allowed to remain in contact with the zinc until a thick spongy coating of the reduced metal was obtained. The following are some of the results:—

Nitre taken.	Nitre found.
0·05172 gram.	0·0516 gram.
—	0 0520 ,,
—	0 0518 ,,
—	0·0516 ,,
—	0·0517 ,,
—	0·0512 ,,

In the final determination only 2 grams of sheet zinc were used, covered, however, with a thick coating of spongy copper.

4. *Calcium nitrate* in solution decomposes with equal readiness on boiling with zinc and copper. 0·6322 gram of marble was dissolved in nitric acid, the liquid was evaporated twice to dryness to expel the last traces of free acid, and the solution was diluted to 250 c.c. 25 c.c. (the quantity employed in each of the following trials) would contain 0·1026 gram CaN_2O_6:—

CaN_2O_6 taken.	CaN_2O_6 found.
0·1026 gram.	0·1028 gram.

The presence of alkaline sulphates and chlorides has no retarding effect upon the decomposition of the nitrate.

25 c.c. of the calcium nitrate solution mixed with 5 c.c. of the solution of sodium chloride and potassium sulphate, and diluted with 25 c.c. distilled water, was boiled for thirty minutes with about 9 grams of zinc covered with spongy copper. Two experiments were made:—

$Ca2NO_3$ taken.	Found.
0·1026 gram.	(1.) 0·1019 gram.
—	(2.) 0·1026 ,,

5. *Lead nitrate*, and therefore in all probability, the nitrates of

silver, *mercury*, *copper*, *thallium*, and in fact of all metals precipitated by zinc, are similarly decomposed, the zinc nitrate which is formed being afterwards reduced. One determination only, however, and with lead nitrate was made. The weighed quantity of the salt was boiled for about two hours with 20 grams of zinc and spongy copper. The experiment gave 0·5419 gram of $PtCl_4.2NH_4Cl$ and 0·0019 gram of Pt :—

$Pb2NO_3$ taken.	Found.
0·4053 gram.	0·4051 gram.

6. Of all the nitrates experimented upon, the most difficult of reduction appears to be *ammonium nitrate*. From the irregularity of the results at first obtained, I was inclined to believe that the decomposition was incomplete, or that hydroxylamine might be formed, or possibly Divers' hyponitrous acid. Direct experiments, however, have failed to point out the formation of these substances. The discordances appear to depend upon differences in the strength of the solution and the amounts of zinc and copper taken. If the solution is too strong, nitrogen dioxide is evolved, and if the amount of zinc and copper be insufficient the reduction is incomplete.

0·2140 gram NH_4NO_3 gave 1·1805 gram $PtCl_4 2NH_4Cl$ and 0·0034 gram Pt, on boiling with 40 grams of zinc and copper for three hours :—

Percentage amount of total nitrogen.	
Found.	Calculated.
34·81	35·00

7. The mixture of zinc and copper appears to have but a very slight action upon *urea*.

0·1094 gram of this substance (prepared from ammonium cyanate) was dissolved in about 70 c.c. of water in contact with 20 grams of thin sheet zinc covered with spongy copper. The mixture was allowed to stand for about 18 hours in the cold, and was then boiled for two hours.

The distillate gave 0·0110 gram $PtCl_4 2NH_4Cl$ and 0·0005 gram Pt :—

Calculated amount of nitrogen.	Found.
46·66 per cent.	0·69 per cent.

0·2137 gram of urea was dissolved in 10 c.c. of water in contact with about 20 grams of zinc and copper, and the solution was boiled down to dryness. A small quantity of water was then added to the flask, and the liquid was again evaporated to dryness, this process being repeated three or four times. The distillate gave 0·0255 gram $PtCl_4.2NH_4Cl$:—

Calculated N.	Found.
46·66 per cent.	0·74 per cent.

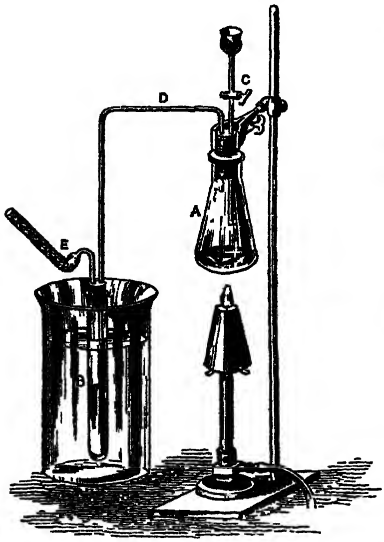
If the urea had been completely decomposed, the above quantity should have given 1·588 gram of the platinum salt. The minute quantity of ammonia found might be due to a trace of ammonium salt in the urea, arising from the mode of its preparation, or, which is more probable, since the substance was recrystallised five times from alcohol, it may have been produced by the gradual decomposition which urea is known to experience by long-continued boiling with water.

8. The readiness with which aqueous solutions of nitrates and nitrites yield ammonia by the action of zinc and spongy copper, would appear to indicate that this reaction might be usefully applied to the determination of these substances when present in drinking waters. It is an objection to the aluminium or zinc and iron methods, as applied to water analysis, that, unless great care is taken, a far larger quantity of nitrates may be introduced in the potash or soda which is needed in such large proportion, than is actually present in the water. Moreover, the strong alkaline solution is extremely liable to froth over on distilling, and if the disengagement of the hydrogen is active, it is almost impossible to boil it without portions of the turbid liquid finding their way into the distillate; and a turbid distillate is of course fatal to the determination of ammonia by Nessler's test.

As the zinc and copper process presents none of these disadvantages, I have sought to make the process applicable to water analysis.

The following is a convenient and expeditious method of operating. The weighed residue in the platinum dish obtained in the determination of the total soluble matter in the water is treated with 10 or 12 c.c. of water, to which a small piece of previously ignited lime about the size of a hemp-seed is added, and the liquid is gently boiled until about 4 or 5 c.c. only remain. The primary object in adding the lime is to facilitate the evolution of the ammonia. A very dilute solution of nitre was boiled with zinc and copper, until ammonia could no longer be detected in the distillate by Nessler's solution; the volume of the liquid required to be distilled was about 120 c.c. When the same quantity of nitre solution was boiled with the previous addition of a minute fragment of lime, but otherwise under the same conditions as before, all the ammonia came over in the first 25 c.c. of the distillate. Three or four grams of thin sheet zinc (that used in all the experiments described was about 0·084 mm. in thickness; 1 gram would therefore expose a surface of 17·89 mm.) previously cleaned by a little dilute acid, and cut into small pieces, are placed into the flask A, which has a capacity of 100 c.c. The zinc is covered with a moderately concentrated solution of copper sulphate, which is allowed to act until a thick dark brown spongy covering of copper is precipitated. The metals are washed four or five times by decantation with cold water, care being taken to detach the copper particles as slightly as possible from the zinc. At the last,

washing the water is drained away as far as practicable. The nitrate solution is transferred from the platinum dish, and the last portions are rinsed out by a few c.c. of cold water, until the liquid in the flask amounts to 25 or 30 c.c. A caoutchouc stopper is then inserted; this is pierced with two holes, through one of which passes a funnel-tube, provided with a well-fitting glass stopcock C, through the other passes the tube D, bent twice at right angles and ending in the wide test-tube B, which is also fitted with a caoutchouc stopper. The tube B has a capacity of about 60 c.c.; it is 18 cm. long, and is graduated to hold 50 c.c. The tube E is partially filled with well-washed fragments of glass. Before inserting the stopper, one drop of pure dilute hydrochloric acid is placed in B, together with 2 or 3 c.c. of water; the glass in the bent tube E is also moistened with two drops of the dilute hydrochloric acid. The liquid in the flask is now caused to boil, to decompose the nitrate; the escaping steam and ammonia condense in B, which is cooled



by immersion in cold water. Any ammonia that may escape condensation in B is retained in the bent-tube E. The liquid in the flask is evaporated nearly to dryness, the lamp is drawn aside, and the funnel is filled with boiling distilled water, the stopcock is opened, and the water is permitted to run into the flask. This process is repeated until B contains about 40 c.c. of water. The lamp is now drawn aside, and the tube E is filled with water; as the steam condenses in the flask the water is of course driven into B; by refilling the tube once or twice, the fragments of glass will be thoroughly washed. B is detached from the cork, and a second tube containing 1 or 2 c.c. of water acidulated with one drop of hydrochloric acid is placed in its stead; a drop of hydrochloric acid is permitted to run on to the fragments of glass, and the distillation is continued until a second portion of 40 c.c. has passed over. The glass fragments are rinsed, and a third tube is substituted. Unless the nitrates are present in exceptionally large quantity, the first 40 c.c. will contain the whole of the ammonia. The amounts of ammonia contained in the several portions of the distillate are then estimated by Nessler's solution. The contents of the

tubes are diluted until they measure 50 c.c., water being poured into the tube, until its level is coincident with the mark on the glass, and the liquid in each is mixed by agitation with a thin and narrow glass tube, on which a bulb has been blown of sufficient diameter to pass readily into the tube. By drawing the tube up and down once or twice in the liquid, it will be thoroughly mixed. 10 c.c. of the liquid in the first tube are then transferred by means of a pipette to a similar tube, also graduated to hold 50 c.c., and further diluted to the mark with pure water. 1 c.c. of Nessler's solution is added, and in a few minutes the colour is noted. If it is measurable it is then compared in the usual manner with that produced by a standard ammonium chloride solution. If the colour is too dark for accurate comparison, 5 c.c. only of the original liquid are withdrawn; if very light, the remaining 40 c.c. may be used. The intensity of colour given by the first 10 c.c. will indicate the proper quantity to be withdrawn to give the tint which the operator finds by experience to be the best suited for comparison. The standard ammonium chloride solution which I find most convenient to use contains 0·07867 gram NH_4Cl per litre. 1 c c. is equivalent to ·025 mgrm. of ammonia. 5 c.c. (or 110 drops from my burette, which is of Mohr's pattern, with glass stopcock) of this solution may be added to the liquid, before the addition of the 1 c.c. of Nessler's solution gives the least turbidity. To test this method of determining nitrates in water, a solution of nitre was diluted, until 1 c.c. of the liquid contained 0·167 mgrm. KNO_3; the quantity of nitre contained in 10, 15, and 20 c.c. was then determined in the manner described.

	Taken.	Found.
(1.)	10 c.c. = 1·67 mgrm. KNO_3.	1·68 mgrm.
(2.)	10 c.c. = 1·67 „	1·72 „
(3.)	15 c.c. = 2·50 „	2·42 „
(4.)	15 c.c. = 2·50 „	2·49 „
(5.)	25 c.c. = 4·16 „	4·01 „

In each case all the ammonia was contained in the first 40 c.c. of the distillate.

9. This reaction with zinc and copper in presence of water will doubtless admit of many other useful applications. For example, I find that the two metals completely reduce *alkaline chlorates* to the state of chlorides, as the following experiments show :—

I. 0·4990 gram potassium chlorate was dissolved in water, and gently boiled with 15 grams of sheet zinc coated with copper. The liquid was filtered, and the amount of chlorine in solution as chloride estimated by decinormal silver solution and potassium chromate. The liquid required 40·1 c.c. silver solution.

II. 0·2995 gram potassium chlorate treated with 10 grams of zinc and copper, required 20·2 c.c. of silver solution.

Cl found.		
I.	II.	Calculated.
28·52	28·77	28·96

10. *Iodic acid* is in like manner reduced by this treatment.

0·1040 gram ammonium iodate treated with zinc and copper, gave 0·0968 gram silver iodide, and 0·0135 gram metallic silver.

Iodine calculated.	Found.
65·81	65·42

11. The two metals would, in all probability reduce hypochlorous acid with equal readiness: this reaction might constitute a simple method of determining the total chlorine contained in bleaching powder. Zinc and spongy copper when heated with potassium ferricyanide reduce that salt to potassium ferrocyanide. Messrs. Gladstone and Tribe have already remarked that the metals act on chloroform and ethyl iodide. The metals, however, have no action on hyposulphites, phosphates, and arseniates. A solution of codeine boiled with zinc and copper evolves no ammonia.

12. If the amount of substance to be reduced is at all considerable, it is by no means a matter of indifference how much copper is deposited upon the zinc. The quantity of hydrogen eliminated from water by the action of the metals depends to a certain extent upon the quantity of copper present, as the following experiments show:—

I. 9 grams of sheet zinc were coated with a *thin* film of coherent copper: on boiling with water for one hour, 148·2 c.c. of hydrogen, measured at 0°, and 760 mm. were evolved.

II. 9 grams of zinc covered with a bulky deposit of copper gave 484·3 c.c. of hydrogen at 0°, and 760 mm. after boiling for one hour with water.

Moreover the *condition* of the copper is of importance; brass, however finely divided, is without reducing action upon nitrates. Indeed, the spongy copper *alone* is able to reduce small quantities of nitrates. A thick sheet of zinc was immersed in copper sulphate solution, and the precipitated metal was rinsed into the distilling flask A (Fig. 1) by the aid of the wash-bottle. 20 c.c. of the standard nitre solution (par. 8) was then boiled with the copper, and the amount of ammonia evolved was determined by Nessler's solution.

KNO_3 taken.	Found.
3·34 mgrm.	3·22 mgrm.

4·73 grams of spongy copper boiled with 0·098 gram of nitre gave

0·1667 gram of double chloride of platinum and ammonium and ·0040 gram metallic platinum. This would be equal to 0·0797 gram of nitre; or 81 per cent. of the salt was decomposed.

My thanks are due to Mr. James B. Hannay for his assistance in many of the experiments described in this communication.

XXII.—*Isomeric Terpenes and their Derivatives.* Part I.

By C. R. A. Wright, D.Sc., London, Lecturer on Chemistry in St. Mary's Hospital Medical School.

The experiments detailed below were commenced some two years ago in the hope of obtaining some insight into the nature of the internal differences which exist between the various members of the terpene family.

In order to obtain two well-marked isomerides as subjects for the first series of experiments, the terpenes occurring in the essential oils of nutmeg and orange-peel were chosen, firstly because Gladstone found their boiling-points to be 167° and 174° respectively (*Chem. Soc. Journ.* [2] ii, 1, and x, 1), wherefore it appeared that both substances are different from oil of turpentine (boiling at 160°), and secondly because the comparatively low price of these oils renders it more easy to obtain genuine specimens.

The oils used were obtained from Messrs. Piesse and Lubin, and were not only believed by Dr. S. Piesse to be pure and unadulterated, but were found, by careful proximate analysis and fractional distillation, to be at any rate free from fatty oils, and from turpentine.

§ 1. *Oil of Nutmeg. Proximate Constituents.*

About a kilogram of oil was slowly distilled; the greater part came over below 200°, but some distilled at 290°, a soft brown resin being left in the retort. This constituted 2 per cent. of the oil and gave on analysis carbon 77·9, hydrogen 9·4, agreeing with the formula $C_{40}H_{56}O_5$.

The highest portions of distillate obtained, viz., at 260°—280° and 280°—290°, gave respectively carbon 73·1, hydrogen 7·9, and carbon 72·9, hydrogen 8·1, agreeing with the formula $(C_{10}H_{13}O_2)_n$.

The lower portions of the first distillate were several times fractionally distilled, with the result of producing a considerable quantity of a mixture of hydrocarbons boiling below 180° and a small quantity

of an oxidised constituent boiling above 210°, apparently the "myristicol" of Gladstone. After several fractionations, however, it became evident that this substance alters by the action of heat, becoming changed first into fluids of the same composition, but higher boiling point, and finally into a semi-solid resin not volatile at 300°. The purest myristicol obtained boiled at 212°—218°; this substance, and the higher polymerides obtained by repeatedly distilling it, gave on analysis numbers approximating more closely to the formula $C_{10}H_{16}O$ than to any other probable formula.

(1.) Myristicol boiling at 212°—218°—
0·3005 gave 0·868 CO_2 and 0·280 H_2O.

(2.) Another specimen—
0·2450 gram gave 0·7035 CO_2 and 0 228 H_2O.

(3.) Portion of boiling point 250°—265°, obtained from (1) by repeated distillation—
0·2325 gram gave 0·674 CO_2 and 0·215 H_2O.

(4.) Resin not volatile at 300° obtained from (1) by repeated distillation—
0·2530 gram gave 0·737 CO_2 and 0·229 H_2O.

	Calculated.		(1.)	(2)	(3.)	(4.)
C_{10}	120	78·94	78·8	78·3	79·1	79·4
H_{16}	16	10·53	10·3	10·3	10·3	10·1
O......	16	10·53				
$C_{10}H_{16}O$	152	100·00				

From these numbers it appears that "myristicol" contains as principal constituent a body isomeric with camphor, but differing from that substance in its physical properties, and notably in its power of becoming polymerized by heat. In a future paper it will be shown that both myristicol and camphor are alike in some respects, inasmuch as by the action of phosphorus pentachloride they give rise to chlorinated products, $C_{10}H_{15}Cl$, which split up by heat into hydrogen chloride and ordinary cymene.

The hydrocarbons boiling below 180°, separated from the nutmeg oil by fractional distillation as above mentioned, were heated for some time in contact with sodium, and then submitted to a careful fractional distillation over that metal for some weeks; finally the whole was almost entirely split up into two portions, one constituting about three-fourths of the whole, and boiling at 163°—166°, and the other (about one-sixth as much in bulk) boiling at 173°—177°. Intermediate fractions were at first obtained, but by successive distillations these split

up almost wholly into the higher and lower portions. A small quantity (less than 1 per cent. of the oil employed) boiled at temperatures above 179°; but this appeared to contain a trace of an oxidized ingredient not destroyed by the action of the sodium. Thus the following numbers were obtained:—

(A) Fraction at	163°—164° (the great majority)	0·3305 gram	gave	1·2305 CO	and	0·407	H_2O.
(B) ,,	164°—166° (a considerable quantity)	0·2295	,,	0·7430	,,	0·2495	,,
(C) ,,	173°—175° (a few c.c.'s only)	0·3460	,,	1·1210	,,	0·3645	,,
(D) ,,	175°—177° (second maximum)	0·2930	,,	0·9460	,,	0·3060	,,
(E) ,,	177°—179° (a few c.c.'s only)	0·2590	,,	0·8370	,,	0·2720	,,
(F) ,,	179°—181° (a few drops only)	0·2530	,,	0·8095	,,	0·2770	,,
(G) ,,	181°—185° (ditto)	0·2765	,,	0·8800	,,	0·2980	,,

	(A.)	(B.)	(C.)	(D.)	(E.)	(F.)	(G.)
Carbon	88·24	88·28	88·35	88·04	88·12	86·58	86·80
Hydrogen....	11·89	12·08	11·71	11·61	11·67	12·07	11·98
	100·13	100·36	100·06	99·65	99·79	99·65	98·78

The formula $C_{10}H_{16}$ requires carbon 88·23, hydrogen 11·77, and the formula $C_{10}H_{14}$ requires carbon 89·55, hydrogen 10·45.

These numbers indicate that, contrary to Gladstone's experiments, the hydrocarbon of oil of nutmeg is not a single body boiling at 167° and of formula $C_{10}H_{16}$, but a mixture of a terpene boiling at 163°—164° (corrected temperature) and a hydrocarbon, apparently cymene, boiling towards 177°.

The lowest fractions are not necessarily free from cymene, as the presence of even 14 per cent. of this hydrocarbon would scarcely modify the percentages of carbon and hydrogen. Thus—

$6C_{10}H_{16} + C_{10}H_{14}$ (14 per cent. cymene) requires $C = 88{\cdot}42$; $H = 11{\cdot}58$.

the higher fractions, however, contain a large amount of this hydrocarbon, as—

$2C_{10}H_{16} + C_{10}H_{14}$ (33 per cent. cymene) requires $C = 88{\cdot}67$; $H = 11{\cdot}33$.

The cymene thus contained was isolated by a process suggested to the writer by Dr. Hugo Müller, viz., treating the mixture with sulphuric acid so as to polymerize the terpene present, and then diluting with water and distilling in a current of steam. Perfectly pure cymene was thus obtained. The experiments relating to this substance will be given in a future communication. About 8 per cent. of *pure* cymene was actually obtained from the fraction boiling at 163°—164°, 12 or 14 per cent. being present, whence it appears that the circumstance that a hydrocarbon boiling between 160° and 170° gives numbers agreeing fairly with the formula $C_{10}H_{16}$ is no proof that it is a homo-

geneous substance, that it does not contain several percentages of another hydrocarbon of different formula, *e.g.*, cymene.

On subjecting oil of turpentine to the same treatment, cymene has also been isolated from this substance, whence it appears that there is no proof that terpenes yield terephthalic acid by oxidation, the small quantities of that substance obtained by oxidising oils of turpentine, lemon, &c., being probably derived from cymene pre-existing in the oils; and hence the arguments proving that terpenes are in any way connected with benzene are not so numerous as supposed.

§ 2. *Oil of Orange-peel. Proximate Constituents.*

On distilling about half a kilogram of the oil it was found to commence boiling at 175°; 97·2 per cent. came over below 180°; the remaining 2·8 per cent. constituted a soft resin containing carbon 75·6, hydrogen 9·7, agreeing with the formula $C_{20}H_{30}O_3$. A few drops passed over between 180° and 280°; the portion collected at 240°—250° contained carbon 76·7, hydrogen 10·9, agreeing with the empirical formula $C_{40}H_{64}O_5$. The portion passing over at 210°—230° appeared to be identical with myristicol, as it gave numbers agreeing with the formula $C_{10}H_{16}O$. Like myristicol it became polymerised by repeated heating, becoming transformed into an isomeric resin. This contained carbon 79·7, hydrogen 10·6. Owing to the extremely small proportion in which this constituent exists, it was not found practicable to obtain it in an absolutely pure state, and hence it is probable that the only appreciable point in which it differed from myristicol, viz., odour, was caused by the presence of a small amount of some other substance.

From the apparent presence of a minute quantity of myristicol in orange-peel oil it might be perhaps expected that cymene might be contained in the hydrocarbon present in that oil; this does not, however, appear to be the case, *as no terephthalic is obtainable from that hydrocarbon by oxidation.* After several distillations over sodium, the orange-peel hydrocarbon boiled quite constantly at 178° (corrected; Gladstone found 174°) and gave the following numbers :—

0·4135 gram gave 1·3370 CO_2 and 0·4495 H_2O.

	Calculated.		Found.
C_{10}	120	88·23	88·17
H_{16}	16	11·77	12·08
$C_{10}H_{16}$	136	100·00	100·25

Evidently, from its boiling point, this hydrocarbon (termed *hesperidene* by Gladstone) is not identical with the lowest-boiling nutmeg

terpene; similar oxidation-products are, however, obtainable from these two hydrocarbons.

Cymene was carefully sought for in this hydrocarbon by the method formerly described, viz., agitation with several times its weight of strong sulphuric acid, dilution with water after 24 hours' standing, and distillation in a current of steam. 200 grams of hydrocarbon thus treated yielded, as first distillate, about 5 c c. of a hydrocarbon that was much blackened by a second treatment with sulphuric acid; after dilution and distillation, about 2 c.c. of hydrocarbon were obtained; this was treated a third time with sulphuric acid which still blackened it much; after distillation less than 1 c.c. was obtained; this was carefully oxidised by chromic solution, but no trace of terephthalic acid was produced; it is hence pretty evident that no appreciable quantity of cymene could have been present in the hydrocarbon.

It is noteworthy that the heat developed by agitating hesperidene with sulphuric acid is sensibly less than that produced by similarly treating the same quantities of sulphuric acid and the nutmeg hydrocarbon (A), boiling at 163°—164°, notwithstanding that this latter contains a considerable quantity of cymene which is not acted on. It was not found practicable to make any accurate determination of the amounts of heat actually given out; without doubt the difference in boiling point and in other properties, physical and chemical, of the two hydrocarbons is closely connected with the different amounts of potential energy thus apparently contained in equal weights of the bodies in question. The same phenomenon is noticeable when bromine is dropped into the two hydrocarbons; the nutmeg product developes much more heat than that from orange oil, combination to dibromides of formula $C_{10}H_{16}Br_2$ being the main reaction in each case.

§ 3. *Action of Potassium Dichromate and Sulphuric Acid on the Hydrocarbons.*

A. Hesperidene

The hesperidene employed was carefully distilled a large number of times over sodium, and *wholly* volatilised in an atmosphere of hydrogen below 179°. Several ounces of this pure hydrocarbon were submitted, in quantities of about half an ounce at a time, to the action of a large volume of 10 per cent. solution of potassium dichromate, enough sulphuric acid being added to saturate the metals of that salt; about a litre of solution being used to every 10 c.c. of hydrocarbon, and the whole being boiled for several days in a flask with an inverted condenser attached; much CO_2 was evolved, and the oil diminished greatly in volume and became somewhat viscid: on careful examination of the chrome liquors, no trace of toluic or of terephthalic acid was found to

be produced in any case. The unattacked oil had a powerful odour of *mint*, which became more like that of *anise* on standing for some months: it was separated by a funnel, washed, and distilled; the greater part came over below 180°, and smelt like orange oil with a minty odour; a portion, however, was left, and did not wholly distil at the limits of the mercurial thermometer. This portion of higher boiling point resembled the similar mixtures obtained from nutmeg oil and pure orange oil, inasmuch as it appeared to consist chiefly of a portion boiling near 215°, of formula $C_{10}H_{16}O$, acquiring a higher boiling point without appreciable change of composition on continued heating; it had a powerful smell of mint when fresh.

The total quantity of the portion of higher boiling point thus obtained was very small, not constituting more than 1 per cent. of the hydrocarbon employed; it was not, however, precontained in the hydrocarbon used, as this was *wholly* volatile below 179°.

The following numbers were obtained:—

A. Portion unattacked by chrome liquor fractionally distilled until all boiling below 210° was separated.
Portion boiling at 210°—220°.
0·170 gave 0·487 CO_2 and 0·1335 H_2O.

B. Similar portion from another set of experiments.
0·301 gave 0·869 CO_2 and 0·272 H_2O.

C. A and B mixed together, and distilled several times, acquired a higher boiling point, a few drops distilling at 240°—250°, and a little resin not volatile at 300° being left in the retort.

Distillate at 240°—250°. 0·1945 gave 0·561 CO_2 and 0·174 H_2O.

	Calculated.		Found. A.	Found. B.	Found. C.
C_{10}	120	78·94	78·1	78·7	78·7
H_{16}	16	10·53	10·0	10·1	10·0
O	16	10·53	—	—	—
$C_{10}H_{16}O$ ..	152	100·00			

The above results indicate that by the oxidizing action of chromic solution on hesperidene, a portion of the hydrocarbon becomes transformed into a body which, if not identical with myristicol and with the camphor contained in small proportion in orange-peel oil, differs from them only in the matter of odour, *i.e.*, that a hydrocarbon has been transformed by direct oxidation into a body which appears to possess the nature of an alcohol.

The majority of the hydrocarbon employed in the above experiments

appeared to be completely oxidized to carbonic acid and water. On distilling the chromic liquors, an acid distillate which reduced silver salts on boiling was obtained: the barium salt of the contained acid was made, and from it the silver salt by precipitation with silver nitrate. After recrystallisation from boiling water the silver salt gave numbers showing that the acid was pure acetic acid.

0·309 gram gave 0·2000 Ag.

Silver found..........	64·7 per cent.
Calculated for acetate..	64·7 per cent.

Acetic acid, therefore, and probably a trace of formic was produced; the quantities of these acids found, however, bore a very small proportion to the hydrocarbon oxidized.

Berthelot has shown that when camphene is oxidized by platinum black, there is produced a small quantity either of camphor or of an isomeride thereof by the direct addition of oxygen—

$$2C_{10}H_{16} + O_2 = 2C_{10}H_{16}O$$

(*Jahresbericht*, 1858, 441).

The resinizing of hydrocarbons from essential oils on keeping is probably due to the gradual absorption of oxygen and the polymerization of the $C_{10}H_{16}O$ products thus formed.

In order to be perfectly certain that terephthalic acid is not a product of the *complete* oxidation of hesperidene, 50 grams of hydrocarbon were completely oxidized by boiling for several days with a mixture of 2 parts potassium dichromate and 3 of strong sulphuric acid with a bulk of water equal to three times that of the acid: *no trace of terephthalic acid was produced.*

B. Lowest-boiling Hydrocarbon of Nutmeg Oil.

The lowest fraction (163°—164°) of the previously-described nutmeg hydrocarbons was treated with chromic liquors precisely as the hesperidene just described. Carbonic and probably formic acid were produced, together with a small quantity of an acid which had all the characters of terephthalic acid (which, as will be shown in the next section, is producible from this fraction by the action of nitric acid). The apparently unattacked hydrocarbon was found on distillation to contain a small quantity of an oxidized substance closely resembling myristicol, the camphor contained in orange-peel oil, and the isomeride of myristicol (?) obtained by oxidizing hesperidene as above described: the few drops obtained boiled above 210°, and gave the following numbers:—

0·328 gram gave 0·9445 CO_2 and 0·308 H_2O.

	Calculated.		Found.
C_{10}......	120	78·94	78·53
H_{16}	16	10·53	10·43
O	16	10·53	—
$C_{10}H_{16}O$	152	100 00	

The only difference perceptible between these four bodies, each expressed by the formula $C_{10}H_{16}O$, lay in their odours, each one being distinct from the others in this respect; it is hence believed that either all four are essentially identical, the difference in odour being due to very minute quantities of other products present along with the main constituent $C_{10}H_{16}O$; or else that the isomerism between them is very faintly marked, and that there must be some close internal connection between them.

The chromic liquors yielded, on distillation, an acid liquid; this was neutralised by fresh silver carbonate and the silver salt recrystallised from boiling water.

0·5265 gram gave 0·3390 Ag.

Silver found	64·4 per cent.	
Calculated for acetate	64·7	„

With the exception, therefore, of terephthalic acid (which, as previously pointed out, is probably wholly derived from the admixed cymene) the subtances produced by oxidation with chromic solution of hesperidene and of the lowest boiling hydrocarbon of nutmeg oil, are either identical or closely akin, being acetic, formic, and carbonic acids, together with a body of formula $C_{10}H_{16}O$ in each case.

§ 4. *Action of Nitric Acid on the Hydrocarbons.*

A. Hesperidene.

Schwanert has shown (*Ann. Chem. Pharm.*, 128, 77) that when camphor and certain other analogous oxidized substances are treated with nitric acid, there is produced, *inter alia*, a non-crystalline acid, *camphresic acid* = $C_{10}H_{14}O_7$. Kachler, however, finds (*Ann. Chem. Pharm.*, 159, 281) that the so-called camphresic acid from camphor consists essentially of a crystallisable acid of formula $C_9H_{14}O_6$ ($C_9H_{12}O_5$ when dried at 100° or distilled), to which he gives the name of *camphoronic acid:* this is characterised by giving a sandy tribasic barium salt precipitated only on boiling. As Schwanert states that his camphresic acid is also obtainable from certain hydrocarbons of the $C_{10}H_{16}$ family (*e.g.*, from citrene), it might be expected that this acid would be obtainable from hesperidene, and from the nutmeg hydrocarbon; bodies of similar physical character are indeed obtainable, but their

compositions appear to agree neither with camphresic acid nor with camphoronic acid.

On slowly dropping hesperidene into 8 or 10 times its bulk of a boiling mixture of equal volumes of nitric acid and water, a vigorous action takes place, red fumes being copiously evolved, and the hydrocarbon becoming partially transformed into a brown resinous substance which on further treatment partially disappears and becomes yellow: an inverted condenser should be attached to the reaction flask to avoid loss of hydrocarbon.

When the action of the nitric acid has almost ceased, a pale yellow, hard, resinous substance is left, of which a small portion dissolves in ammonia. The undissolved portion gave on analysis carbon 59·3, hydrogen 6·1; nitrogen being also indicated as present by the sodium test.

The ammoniacal solution was dark-red brown in colour; after treatment with purified bone-black the partly decolorised liquid deposited amorphous flakes on supersaturation with nitric acid; these flakes somewhat resembled terephthalic acid, but had a very different composition. On boiling the ammoniacal solution with pure animal charcoal until it was almost wholly decolorised, the filtrate was found to give no precipitate with acids, showing that the whole of the dissolved substance had been taken up by the charcoal. Hence this dissolved portion could not have been terephthalic acid. The following numbers were obtained:—

A. Crude yellow substance precipitated from ammoniacal solution, 0·4065 gram gave 0·687 CO_2 and 0·164 H_2O.

B. Precipitated after most had been decolorised by animal charcoal, 0·232 gram gave 0·406 CO_2 and 0·096 H_2O.

	A.	B.
Carbon	46·1	47·7
Hydrogen	4·4	4·6

Nitrogen was found in specimen A by the sodium test.

Terephthalic acid contains—

Carbon	57·84
Hydrogen	3·61

Even supposing the yellow substance had been pure terephthalic acid, it would have amounted to only 0·2 to 0·3 per cent. of the hydrocarbon used.

From the above results, together with the fact that no terephthalic acid is obtainable by means of chromic liquor, it is inferred that *hesperidene yields no terephthalic acid at all by oxidation.*

The nitric acid solution separated from the undissolved yellow resin was evaporated to dryness on the water-bath, the residue dissolved in

water, filtered, and neutralized by ammonia; barium nitrate added in the cold gave a copious precipitate of *oxalate*, from which the acid was obtained by treatment with sulphuric acid. The crystallised acid was analysed, and the acid recognised by the explosibility of its silver salt, and the examination of its calcium salt.

0·829 gram, dried at 100°, gave 0·569 $CaCO_3$, and on ignition, 0·322 CaO.

Calculated from $CaCO_3$	Ca = 27·4 per cent.
" " CaO	Ca = 27·7 "
The formula $C_2O_4Ca.H_2O$ requires..	Ca = 27·4 "

The filtrate from the barium oxalate when heated to boiling gave a trifling sandy precipitate, but this was found to be nothing but a little barium oxalate; no trace of Kachler's camphoronic acid could be found. Lead nitrate gave a copious yellow precipitate, from which, by means of sulphuretted hydrogen, a syrupy acid was obtained; this acid was soluble in ether, the ethereal solution leaving a thick syrup, which, on standing several months, became semi-solid. No crystals, however, could be obtained from the mass either by pressure in bibulous paper or by washing with small quantities of water, &c. This product, however, was not perfectly homogeneous; on boiling with marble powder it furnished a neutral solution, which yielded by evaporation an amorphous gummy calcium salt containing 17·0 and 17·2 per cent. calcium when dried at 100°, and 18·1 and 18·1 per cent. when dried at 160°.

This calcium salt was dissolved in water and precipitated by addition of alcohol, which threw down bulky amorphous flakes; the filtrate from these evaporated to dryness gave a very hygroscopic calcium salt fusible at 100°, and decomposing with emission of a peculiar odour at higher temperatures.

0·593 gram, dried at 100°, gave 0·140 $CaSO_4$. Ca = 6·94 per cent. The precipitated calcium salt dried up to a gum-like mass and yielded the following numbers:—

0·4785 gram dried at 100° lost 0·0540 at 160° and gave 0·301 $CaSO_4$.

0·5865 gram dried at 160° gave 0·4120, $CaSO_4$.

The salt dried at 160° gave...... calcium	= 20·85 per cent.
" " "	= 20·67 "
" at 100° "	= 18·50 "
Moisture lost at 160°	= 11·28 "

The acid was obtained from this calcium salt by addition of sulphuric acid to its solution and extraction with ether; a syrup was thus obtained which became a mass of minute crystals on standing over sulphuric

acid for some months; on solution in water, however, no crystals could be obtained, but only a syrup becoming crystalline after several weeks only.

The following numbers were obtained:—

Acid dried over sulphuric acid for three months—

A. 0·3190 gave 0·483 CO_2 and 0·155 H_2O.
B. 0·4555 gave 0·701 CO_2 and 0·2185 H_2O.

Acid dried at 100°—

C. 0·4150 gave 0·670 CO_2 and 0·196 H_2O.
D. 0·5190 gave 0·8535 CO_2 and 0·2385 H_2O.

Calculated.			Found.		Calculated.			Found.	
			A.	B.				C.	D.
C_{20}	240	41·81	41·29	41·97	C_{20}	240	44·61	44·03	44·85
H_{30}	30	5·23	5·39	5·33	H_{26}	26	4·83	5·25	5·11
O_{19}	304	52·96	—	—	O_{17}	272	50·56	—	—
$C_{20}H_{26}O_{17}.2H_2O$	574	100·00	—	—	$C_{20}H_{26}O_{17}$	538	100.00	—	—

The calcium salt, $C_{20}H_{20}Ca_3O_{17}$, requires 18·41 per cent. calcium.
Found 18·50 " "

At 160° this salt loses $4H_2O$, becoming $C_{20}H_{12}Ca_3O_{13}$.

Calculated percentage of calcium	20·69	per cent.
Observed ditto	20·85	"
	20·67	"
Calculated loss .... =	11·04	"
Observed .... =	11·28	"

It is hence evident that this acid is identical neither with camphresic acid nor with camphoronic acid, these acids requiring the following numbers:—

	Camphresic $C_{10}H_{14}O_7$.	Camphoronic $C_9H_{14}O_6$.	$C_9H_{12}O_5$.
Carbon	48·78	49·54	54·00
Hydrogen	5·69	6·42	6·00

$C_{10}H_{11}Ca'_3O_7$ requires 19·80 p. c. Ca. | $C_9H_9Ca'_3O_5$ requires 23·34 per cent.
$C_9H_{10}Ca'_2O_5$ " 16·81 "

To indicate its origin and its mode of formation (analogous to that of camphresic acid) it is proposed to term this acid *hesperisic acid.*

(B.) Lowest boiling fraction from nutmeg oil.

On treating this fraction in the above described manner results are

obtained precisely similar to those observed with hesperidene; a much larger quantity of resinous matter unattacked by nitric acid is, however, formed, and of this the majority is soluble in ammonia. After decolorisation by animal charcoal, a perfectly white precipitate is obtained on adding nitric acid to the ammoniacal solution; this consists of a mixture of toluic and terephthalic acids.

In a carefully conducted experiment 105·8 grams of hydrocarbon gave 14·0 of purified mixture, or 13·2 per 100 of hydrocarbon; as previously pointed out, these acids are probably produced from cymene still retained by the hydrocarbon in spite of long continued fractional distillation. This mixture gave on analysis 59·8 per cent. carbon, and 4·7 per cent. hydrogen, agreeing with the mixture, $4C_8H_6O_4 + C_8H_8O_2$, which requires carbon 60·0 per cent., hydrogen 4·0 per cent.

In another experiment where the fractional distillation had not been carried so far, and where consequently a larger proportion of cymene was contained, 15·7 parts of mixed acids per 100 of hydrocarbon were obtained, the mixture containing $4C_8H_8O_2 + 3C_8H_6O_4$.

Found, Carbon = 64·3 and 64·2 per cent. : calculated 64·5
„ Hydrogen = 5·1 and 4·9 „ : „ 4·8

It was found extremely difficult to effect a satisfactory separation of the two acids: in boiling water or alcohol toluic acid readily dissolves, whilst terephthalic acid is almost insoluble in these menstrua; in the case of a mixture of the two acids, however, a considerable amount of terephthalic acid is taken up by the toluic acid solution, whilst on the other hand a certain quantity of toluic acid is always left behind in the undissolved terephthalic acid, even after many treatments with boiling water or alcohol.

Even the purest toluic acid obtained after ten crystallisations from boiling water, retained about 20 per cent. of terephthalic, containing carbon, 67·6; hydrogen, 5·8 ($4C_8H_8O_2 + C_8H_6O_4$ requires carbon, 67·6; hydrogen, 5·4).

To obtain the terephthalic acid pure, the portion insoluble in boiling water was boiled for 24 hours with a mixture of 3 parts sulphuric acid, 5 of water, and 2 of potassium dichromate; the unoxidized portion was dissolved in ammonia and precipitated by hydrochloric acid several times; a snow-white mass was finally obtained which after drying at 100° gave the following numbers:—

0·3205 gram gave 0·679 CO_2 and 0·110 CO_2.

	Calculated.		Found.
C_8	96	57·83	57·78
H_6	6	3·62	3·88
O_4	64	38·55	—
$C_8H_6O_4$ ..	166	100·00	

The barium salt was also made—

0·515 gram gave 0·3935 $BaSO_4$.

Ba.	= 44·9
Calculated	= 45·5

This acid exhibited no tendency to melting when heated, but sublimed unaltered; it was carefully examined to see if any small trace of an acid isomeric with terephthalic acid was present; the barium salt, however, yielded nothing but unaltered terephthalic acid when digested with cold water, filtered, and precipitated by hydrochloric acid; similarly nothing but terephthalic acid was dissolved by boiling water. It hence appears that the toluic acid produced simultaneously with the terephthalic acid is only ordinary toluic acid yielding terephthalic acid by further oxidation, which might be expected, as both acids are probably derived from cymene in the hydrocarbon used.

The nitric acid filtrate from the crude toluic and terephthalic acids was treated precisely as the corresponding filtrate from the oxidation of hesperidene. A quantity of barium oxalate was thus obtained from which the calcium salt was prepared as before.

0·372 gram gave 0·259 $CaCO_3$ (after being dried at 100°).

Found. . . . . Ca =	27·8 per cent.
Calculated for CaC_2O_4,H_2O.	27·4 per cent.

No trace of Kachler's camphoronic acid could be obtained from the filtrate from the barium oxalate; after conversion into lead salt, decomposition by sulphuretted hydrogen, and extraction with ether, a sour syrup was obtained very similar to that obtained from hesperidene; this was converted into calcium salt, and the solution precipitated by alcohol; the precipitated calcium salt resembled the one similarly obtained from hesperidene, but yielded the following numbers:—

(A) 0·5380 gram dried at 100°, lost 0·031 at 160°, and gave 0·342 $CaSO_4$.

(B) 0·5260 gram dried at 100°, lost 0·0315 at 160°, and gave 0·334 $CaSO_4$.

	(A.)	(B.)
Percentage of calcium in salt dried at 100°	18·70	18·67
„ „ „ 160°	19·84	19·86
„ water lost at 160°	5·76	5·99

From this precipitated calcium salt the acid was obtained by treatment with sulphuric acid and ether; after drying over sulphuric acid for several weeks, it constituted a viscid syrupy honey-like mass, which gradually became a mass of small crystals closely resembling the acid obtained from hesperidene in appearance.

It yielded the following numbers :—

0·4220 gram lost 0·0280 at 100		Loss = 6·60 per cent.
0·3050 „ „ 0·0210 „		„ = 6·88 „
0·3940 gave (after drying at 100°)	0·669 CO_2 and 0·1835 H_2O	
0·2840 „ „ „ „	0·478 CO_2 and 0·138 H_2O	

	Calculated.		Found.	
C_{20}......	240	45·98	46·31	45·90
H_{26}	26	4·98	5·17	5·39
O_{16}......	256	49·04	—	—
$C_{20}H_{26}O_{16}$	522	100·00		

The substance dried over sulphuric acid was, therefore, $C_{20}H_{26}O_{16}.2H_2O$, the $2H_2O$ being lost at 100°.

Calculated loss	6·45
Observed	6·60 6·88

The calcium salt $C_{20}H_{20}Ca_3O_{16}$, requires 18·86 per cent. calcium.

Found (dried at 100°)	18·70	„	„
	18·67	„	„

When dried at 160°, this calcium salt appears to lose $2H_2O$, forming $C_{20}H_{16}Ca_3O_{14}$.

	Loss of H_2O.	Per cent. of Ca.
Calculated	5·66	20·00
Observed	5·76	19·84
	5·99	19·86

It hence appears that the acid formed by oxidizing the lowest nutmeg hydrocarbon with nitric acid (which may be termed *myristisic acid*), although similar to hesperisic acid in composition and properties, is yet not identical with that acid, containing less oxygen; thus the two acids may be contrasted :—

	Myristisic acid.	Hesperisic acid.
Acid dried over sulphuric acid	$C_{20}H_{26}O_{16},2H_2O$	$C_{20}H_{26}O_{17},2H_2O$
„ at 100°	$C_{20}H_{26}O_{16}$	$C_{20}H_{26}O_{17}$
Calcium salt dried at 100° ..	$C_{20}H_{20}Ca_3O_{16}$	$C_{20}H_{20}Ca_3O_{17}$
„ „ at 160° ..	$C_{20}H_{16}Ca_3O_{14}$	$C_{20}H_{12}Ca_3O_{13}$

§ 5. *Action of Hydriodic Acid on Hesperidene.*

It was hoped that by combining hydriodic acid with terpenes, derivatives might be obtained from the products whose characters might

serve to elucidate the isomerism of the original hydrocarbons; the results obtained below with hesperidene, however, do not promise much advantage in this direction.

Hesperidene was brought in contact with gaseous hydriodic acid, which was absorbed in large quantity; the liquid freed from excess of acid by agitation with dilute caustic soda, gave on analysis numbers indicating a compound $C_{10}H_{16}.HI$ mixed with a slight excess of $C_{10}H_{16}$; no crystalline compound could be obtained by cooling or leaving it to stand.

This hydriodide decomposed by exposure to light or on heating, iodine being set free; it appeared to boil at about 220° with decomposition, hydriodic acid being evolved in small quantity; a portion, however, distilled unchanged mixed with regenerated and partially polymerised $C_{10}H_{16}$.

In the hope of adding on hydrogen to the terpene, the hydriodide was treated with phosphorus and water or hydriodic acid, but without success, a negative result only being obtained whether red or yellow phosphorus was employed, and whether the operation was conducted in a flask with an inverted condenser attached, or in a sealed tube heated to 100°, 130°, or 150°; phosphonium iodide and phosphoretted hydrogen were, however, produced in some little quantity, frequently giving rise to explosions. By heating the mixture for several hours in a flask with inverted condenser attached, the whole of the associated iodine was removed, and finally a mixture of phosphorus acids and a colourless oily hydrocarbon boiling at about 150°, was left; this was sparingly soluble in cold alcohol, rather more soluble in boiling alcohol; a sample precipitated from hot alcoholic solution by addition of water gave these numbers—

0·2620 gram gave 0·851 CO_2 and 0 267 H_2O.

	Calculated.		Found.
C_{15}	180	88·3	88·5
H_{24}	24	11·7	11·3
$C_{15}H_{24}$ ..	204	100 0	99·8

Hence it appears that the hesperidene had become partly polymerised by the action of the hydriodic acid, or perhaps by that of the phosphorus acids produced; Gladstone finds (*Chem. Soc. Journ.* [2], x, 1), that *cedrenes* (as bodies of $C_{15}H_{24}$ formula may be conveniently termed), boil at 249° to 260°.

Hesperidene hydriodide prepared as above was dissolved in alcohol and boiled *per ascensum* with the equivalent quantity of silver cyanide for two hours, when almost all the silver compound had become transformed into iodide; the alcoholic solution had a peculiar odour,

recalling that of the nitriles. In the hope of obtaining a new acid by the reactions—

$$C_{10}H_{17}I + AgCN = AgI + C_{10}H_{17}.CN$$
$$C_{10}H_{17}.CN + 2H_2O = NH_3 + C_{10}H_{17}.CO_2H,$$

the alcoholic solution was boiled *per ascensum* with caustic potash for several hours; a copious disengagement of fishy-smelling ammonia ensued, and a minute quantity of the potash salt of a new acid was formed; the greater part of the hydriodide, however, became converted into a dirty brown tarry mass, which could not be purified; probably this was a polymeride = $(C_{10}H_{16})_n$ formed by the splitting up of the nascent acid, $C_{10}H_{17}.CO_2H$.

The potash-salt was dissolved in water and extracted with ether after souring with hydrochloric acid; a small quantity of a non-crystalline, non-volatile acid was obtained, apparently mixed with formic acid, as the liquid reduced silver salts on boiling, but lost that property after evaporation to dryness. Lead acetate gave a flocculent white precipitate which, after thorough washing, contained 54·6 per cent. of lead.

The neutral salt $(C_{10}H_{17}CO_2)_2Pb$	would require lead =	36·3
And the basic salt $(C_{10}H_{17}CO_2)_2Pb,PbO$	„	53·7

This reaction appeared, consequently, so unpromising, that no further experiments have yet been made in connection with it; possibly the hydrochlorides and hydrobromides of the terpenes might give better results.

§ 6. *Conclusion.*

From the foregoing results, it is evident that turpentine oil (b.p. 160), the terpene of nutmeg oil (b.p. 163°), and hesperidene (b.p. 178), are three different isomerides, since the former gives camphresic acid by its oxidation (Schwanert); the number of formulæ conceivable for bodies $C_{10}H_{16}$ is great, but it appears not impossible that many bodies now believed to be different and peculiar terpenes may, like "myristicene," turn out, on closer inspection, to be mixtures, perhaps of previously known bodies. Further experiments on the nature of the isomerism in this series of compounds are in progress.

In conclusion, it gives me great pleasure to return thanks to Messrs. C. H. Piesse and G. H. Beckett, for much valuable assistance rendered during the earlier and later portions of these experiments respectively.

XXIII.—*On New Processes for Mercury Estimation, with some Observations on Mercury Salts.*

By J. B. HANNAY.

WHILE engaged in the analysis of some mercury ores, I had occasion to test most of the processes now in use, and found, by experience, that they were either very tedious or deficient in accuracy. I therefore set about devising a process which might be speedy, and at the same time accurate. A volumetric process, could I devise a satisfactory one, seemed most likely to afford these qualifications. The idea of estimating mercury by voltaic electricity seemed good, and all that was required was to show that it would work well in practice. I therefore took some pains to devise and perfect both methods. I will first describe the volumetric process; the method for estimation by the battery will be given further on.

Of the various chemical reagents tried, potassium cyanide seemed to be the least affected by the presence of other substances, and at the same time the conversion of mercury into cyanide was in every case quite complete. I tried at first to ascertain when the reaction was complete by bringing a drop of solution of potassium hydrate in contact with a drop of the mercury solution, when, if the conversion is complete, it should give no precipitate. It was found, however, that this test did not work well, as it very often gave a slight dimness after the mercury was completely saturated, probably owing to the presence of potassium carbonate. Another objection was that a drop had always to be taken out, and when working with small quantities of mercury, this seriously diminishes the accuracy of the process. It was found that by adding two or three drops of dilute ammonia to a solution of mercuric chloride, a white precipitate was formed, which was completely redissolved when the conversion into cyanide was complete. The point of saturation can be determined with great accuracy, as both the mercury and cyanide solutions are colourless, so that it is easy to detect the slightest dimness. Before the last drop of cyanide is added, the precipitate is so fine, that the liquid appears just as if fluorescent. When, however, the last drop is added, the fluorescence disappears instantaneously, and the liquid is perfectly clear. In making the following determinations, the exact point of saturation was determined by a method similar to that used by Professor Stas in his process for silver estimation by chloride of sodium. A lens, formed of a small glass bulb filled with water, was placed close to the outside of the beaker, so that its focus was inside the liquid. When there was no sunlight, a gas jet was placed near the beaker. As long as there was the slightest dimness, there

appeared a brilliant streak in the liquid, caused by the light striking against the floating particles, but whenever enough cyanide was added to dissolve the precipitate, the lines (caused by the convergence of the rays) entirely disappeared. The point of saturation is thus very easily and accurately determined. For ordinary determinations the lens may be dispensed with, as the eye can detect a very slight dimness, but where great exactness is required this method should be used. To test this process, the following experiments were made:—

Potassium cyanide was dissolved in water, to form a dilute solution. 4·3424 grams of mercuric chloride were dissolved in 250 c.c. of water. A known volume of this solution was poured into a beaker, diluted with water, and a few drops (generally six) of dilute ammonia added. The cyanide solution was then poured in, until the liquid, after stirring, became perfectly clear. In all these experiments a Mohr's burette (with an Erdmann's float) graduated to tenths of a cubic centimeter, was used. The cyanide solution was run in from this burette, until the liquid was nearly clear, then the last few drops were added from a very fine burette, graduated to hundredths of a cubic centimeter; the length occupied by one cubic centimeter being about 150 millimeters. The following are the results:—

Mercuric chloride solution used.	Mercuric chloride.	Potassium cyanide solution used.	Therefore 1 c.c. of cyanide solution equals in mercury.
cubic centimeters.	gram.	cubic centimeters.	gram.
4·0	0·0694	4·22	0·01213
8·1	0·1406	8 56	0·01212
6·0	0·1012	6·33	0·01214
5·0	0·0868	5·26	0·01216
6·0	0·1042	6·33	0 01214
6·0	0·1042	6·32	0 01216
12·0	0·2084	12 66	0·01214
6·0	0·1042	6·34	0·01213
6·0	0·1042	6·32	0 01216
50·0	0·8684	52·85	0·01213

The average of all these experiments is 0·01214 gram. As the same amount of ammonia had been added to each portion in the foregoing experiments, I wished to ascertain if more or less ammonia would affect the results.

Ammonia added.	$HgCl_2$ solution used.	$HgCl_2$.	KCN solution used.	1 c.c. equals in Hg.
	cub. cent.	gram.	cub. cent.	gram.
3 drops dilute	6	0·1042	6·34	0·01213
50 „ „	6	0·1042	6 33	0·01214
Large excess.	6	0·1042	6·34	0·01213

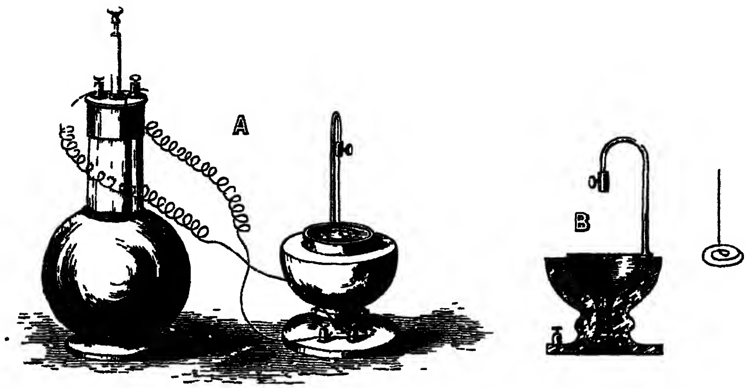
These results show that it does not matter what proportion of ammonia is added. It was found, however, that when the solution is very dilute (less than one part of mercuric chloride in a thousand of water) if a little less cyanide be added than is required for complete saturation, and the liquid agitated for five or ten minutes, it ultimately grows quite clear. This seldom or never makes a difference of more than 0 2 per cent. It shows, however, that the liquid should not be very dilute. The state of dilution, beyond a certain point, does not affect the results in the least, and even when it is very dilute, if the cyanide is run in quickly, and the liquid not stirred very long (not more than one minute at a time), the results are perfectly accurate, as the following experiment shows:—

0·0694 gram of mercuric chloride, dissolved in 200 c.c. of water, took 4·22 c.c. of the standard cyanide solution, which equals 0·0694 gram of mercuric chloride, showing that the results are perfectly accurate, even when the mercuric chloride solution contains only 1 part in 3,000 of water. Concentrated solutions of mercuric chloride also give good results. Take for instance the following experiment:—1·9879 gram of mercuric chloride was dissolved in 50 c c. of water, giving a solution containing about 1 part in 25 of water, or nearly saturated at 15° C. This solution took 120 83 c c. of cyanide solution, which equals in mercury 1·4668 gram, the calculated amount being 1·4667 gram. The mercury solution must not be hot, as in that case it invariably gives results a little too low, and if it is boiled after the addition of ammonia, insoluble compounds are generally formed, so that the cyanide solution seldom renders the mercury solution perfectly clear. The temperature does not affect the results, if kept between 8° and 20°.

As it was necessary that the mercury should be in the state of chloride, I set about to find the best way to obtain the metal in this state, so as to be in a fit state for estimation by cyanide. It was found that on dissolving the sulphide in aqua regia, the whole of the mercury existed as chloride (no sulphate being formed), so that, when mercury is mixed with other metals, it is only necessary to precipitate as sulphides with hydrogen sulphide, and separate the arsenic, copper, &c., by ammonium sulphide and nitric acid, or any process that may be applicable, so as to leave the mercury as sulphide. The sulphide thus obtained is dissolved in a small quantity of aqua regia, diluted and filtered from sulphur, neutralised with potassium hydrate, and after the addition of a few drops of ammonia, the mercury is estimated by standard cyanide. The following are the results of two estimations done after separation of the mercury from mixed solutions:—0·4342 gram of mercuric chloride mixed with cupric and ferric chlorides, after separation, took 26·38 c.c. cyanide solution, which equals in mercuric chloride, 0·4341 gram. Another portion, weighing 0·1736 gram, mixed with antimony, cadmium, and cupric chlorides, took, after separation,

10·55 c.c. cyanide solution, which equals 0·1734 gram of mercuric chloride. It will be seen from these experiments that this process is very satisfactory, being speedy, accurate, and simple.

The battery estimations were conducted as follows:—The apparatus employed is shown in the accompanying figure. A shows the battery in action, as used in performing an experiment. B is a section of the



support for the basin. It consists of a turned copper basin in a wooden support, the copper basin serving as a conductor, on which I place the platinum basin. A piece of platinum wire, coiled horizontally (the outer coil being a little less in diameter than the platinum basin) is used as the positive pole, being connected by a binding screw with the carbon of the battery. The copper basin in which the platinum basin rests is connected with the zinc of the battery. The following are some determinations made by the battery:—

0·4275 gram of mercury was heated with strong sulphuric acid, till the whole was converted into sulphate. This was transferred to the platinum basin, and the connections with the battery completed. The current was allowed to act for about six hours, when it was found that the solution gave no precipitate with stannous chloride, and the mercury was all in the fluid state on the surface of the basin. The basin was filled up with water, and, without disconnecting the battery, the solution was nearly all drawn off with a pipette. This was repeated several times, and the basin finally removed and washed with distilled water, absolute alcohol, and lastly with ether. It was then placed under a bell-jar, in which the pressure was reduced by the air-pump to about 160 mm. It was kept at this pressure for about two minutes, air was then admitted, and the jar again exhausted. This treatment was repeated, and the basin then weighed, when the mercury was found to weigh

0·4276 gram. This gives an excess of one-tenth of a milligram, and so is as accurate as any ordinary balance will weigh.

In the second experiment, 0·5610 gram of mercurous nitrate was converted into mercuric sulphate by treatment with strong sulphuric acid, and treated exactly as above, as far as the precipitation goes; only, instead of washing with ether, it was only washed with absolute alcohol, and dried in a current of air, at about 38°, and weighed when perfectly dry. It gave of mercury 0·3998, the calculated amount being 0·4007, showing a loss of nearly a milligram, or about two-tenths per cent.

0·5200 gram of mercurous nitrate was dissolved in water acidified with nitric acid, reduced directly, without conversion into sulphate, and dried exactly as the foregoing. It gave 0·3702 gram of mercury, the calculated amount being 0·3714, showing a loss of 1·2 milligram, or three-tenths per cent.

0·7359 gram of mercurous nitrate, acidified with nitric acid, and reduced directly as in the foregoing case, but washed with ether and dried *in vacuo*, gave 0·5257 grm. of mercury, the calculated amount being 0·5256 gram. In this case, as in the first experiment, there is an excess of weight only to the small extent of one-tenth of a milligram. The basin and mercury were heated to about 60°, a slow current of air drawn over them for about 6 minutes, and the weight again noted. The mercury weighed 0·5195, showing a loss of 6·2 milligrams from the former weighing, or rather over 1 per cent.

0·5193 gram of mercurous nitrate was reduced as in the foregoing experiment, and the mercury washed with alcohol and dried in a current of air at 100°. After being kept at this temperature for about ten minutes, the mercury weighed 0·3610 gram, the calculated amount being 0·3709, showing a loss of 9·9 milligrams, or over 2·6 per cent.

0·8318 gram of mercurous nitrate treated as before, only washed with absolute alcohol and dried *in vacuo*, gave 0·6090 grm. of mercury. It was then washed with ether and dried *in vacuo*, when it weighed 0·5940. The calculated amount is 0·5940 gram. The first weighing showed an excess of 0·015 gram, or 2·5 per cent. of mercury.

Mercuric chloride is not reduced entirely to the metallic state, as a large portion gets reduced to mercurous chloride, and is not further acted upon, as the following experiment shows: 0·4555 gram of mercuric chloride was dissolved in water, and acidified with dilute sulphuric acid. It was then placed in the battery circuit, and treated exactly as in other cases, that is, dried with ether *in vacuo*. At first it was seen that a good quantity of a white powder was formed, which refused to be reduced even when the power of the battery was augmented. The contents of the basin weighed 0·3829 grm., the calculated amount being 0·3361, showing an excess of 0·0468 gram, or nearly 14 per cent.

It occurred to me that, if the chloride were first converted into cyanide, as in the volumetric process, it might suffer complete reduction.

0·3624 grm. of mercuric chloride was therefore weighed out, and treated with cyanide. It took for saturation 22·03 c.c. of cyanide solution, which equals in mercury 0·2674 gram. The solution after being reduced in bulk by evaporation, was placed in the basin, and the circuit with the battery completed. After being allowed to stand for six hours, it was treated with distilled water, alcohol, and ether, and dried *in vacuo*. It weighed 0·9671 gram. The calculated number and the cyanide determination, both gave 0·9674 gram: there is therefore a loss of only three-tenths of a milligram.

As the sulphate is completely reduced by the battery, I tried to convert the chloride into sulphate by heating with strong sulphuric acid. It was found that, as long as the acid was dilute, no action took place, and when the acid became so concentrated that its boiling point was raised to the temperature at which mercuric chloride volatilises, salt sublimed unchanged. After the excess of salt had been expelled by heat, the sulphuric acid was allowed to cool, and the salt which crystallised out (the solution becoming almost solid), was poured with sulphuric acid on an asbestos filter, and allowed to drain for three days, the moisture taken up by the sulphuric acid serving to carry the excess of acid through the filter. The salt was then washed with very small quantities of cold water, and dried between the folds of bibulous paper, then allowed to dry over sulphuric acid for two days. The salt which sublimed was purified in the same way. Both were analysed, and yielded as follows:—

	Sublimed.	Crystallised.	Calculated.
Mercury, Hg	73·820	73·799	73·801
Chlorine, Cl_2	27·177	26·280	26·199
	100·997	100·079	100·000

This clearly shows that mercuric chloride dissolves without decomposition in strong sulphuric acid. The acid seemed to dissolve nearly half its own weight.

The mercury was estimated by cyanide solution and the chlorine as silver chloride. It is thus seen that mercury has a stronger affinity for chlorine than for sulphuric acid. This is also seen when mercuric sulphate is heated with hydrochloric acid, mercuric chloride and free sulphuric acid being formed. It was found that when mercury is heated with strong sulphuric acid, the resulting sulphate (although decanted from the unoxidised metal), on treatment with hydrochloric acid, gave from one-third to one-fourth of its weight of mercurous

chloride, showing that mercurous sulphate was formed at the same time as the mercuric salt. When, however, the whole of the mercury was converted into sulphate and the solution heated for a minute or so after, the resulting salt dissolved entirely in hydrochloric acid as mercuric chloride, showing that it existed entirely as mercuric sulphate. The formation of mercurous sulphate is due to the action of the sulphur dioxide evolved, as this substance in solution reduces at once both mercurous and mercuric sulphates and nitrates, partly to the metallic state, and partly to lower salts. By the aid of heat, however, they may generally be all reduced to the metallic state. Sulphurous acid does not at once reduce mercuric chloride, but after a little a white precipitate of mercurous chloride is formed. It was found, however, that, even after long standing and with a large excess of sulphurous acid, the reduction was never quite complete. Mercuric cyanide is not reduced at all by sulphurous acid.

It was noticed in the volumetric process, when only one or two drops of dilute ammonia were added to the mercury solution, that on adding the cyanide solution, the precipitate caused by the ammonia steadily increased, till about half the required amount was added, and from that point it was slowly dissolved by the further addition of cyanide. It was also noticed, that when a large quantity of ammonia was added, the precipitate began to dissolve from the first addition of cyanide, but if the two solutions be compared when about half the required amount of cyanide has been added, they will be found to be of nearly the same degree of opacity, provided of course, they are of the same degree of dilution. It was thought that the precipitates might be nearly the same in composition, so the following experiments were made to ascertain this.

14 c.c. of mercury solution (of the strength mentioned in the first part of this paper) were taken in each case, and diluted with 150 c.c. of water. To one portion five drops of dilute ammonia were added, to the other a large excess. 7 c.c. of the cyanide solution were run into each, that amount being about half the quantity required for saturation. The precipitate was allowed to settle, collected on a weighed filter, and dried over strong sulphuric acid for four days, then weighed. The precipitate in the portion with only five drops of ammonia weighed 0·0689 gram, and contained 16·5 per cent. of mercury, while the precipitate in the one with excess of ammonia weighed 0·1070 gram, and contained 78·5 per cent. of mercury, showing that the two precipitates have entirely different compositions.

It is well known that when a solution of mercuric chloride is evaporated, a portion of the salt is volatilised with the aqueous vapour. I have found that this takes place when a solution containing as little as one part in 500 of water is boiled, but when the solution is more dilute, no mercury could be detected in the distillate. I have also

found that a solution of mercuric chloride, containing as much as one part in 20 of water, can be boiled without loss of mercury, provided it be acidified with dilute hydrochloric acid. When, however, the hydrochloric acid begins itself to be volatilised, considerable quantities of mercury may be detected in the distillate. In dissolving mercuric sulphide, it was found that, if the aqua regia was not very strong and was not boiled after the mercury sulphide was dissolved, no mercuric chloride could be detected in the washings of the gases evolved. Sulphuric acid has no effect either in retarding or accelerating the volatilisation of mercuric chloride. To show how much loss is caused by evaporating a solution of mercuric chloride, the following experiment may be taken. 0·4306 gram of mercuric chloride dissolved in 25 c.c. of water and evaporated to dryness on a steam-bath, left a residue of 0·4057, showing a loss of 5·76 per cent. I may mention, in connection with this subject, that when solutions of mercuric chloride are evaporated or boiled in a room, even when well ventilated, the salt which is thus thrown into the atmosphere is very injurious to the human system; in fact, all the symptoms of mercury poisoning are strongly manifested.

When it was seen that mercuric chloride was so volatile, experiments were made to find the best process by which metallic mercury might be converted into chloride for estimation, and at the same time to dispense with a condensing apparatus. It was found that, on dissolving mercury in aqua regia, considerable quantities of mercury were found in the distillate. When mercury was dissolved in hot nitric acid without actual boiling, no mercury could be detected in the washings of the evolved gases, so that mercury can be converted into chloride by dissolving in hot nitric acid and then gently heating with hydrochloric acid. By numerous experiments, I have found that by this method no loss of mercury is sustained. On converting mercury into sulphate by heating with strong sulphuric acid, no mercury was found in the washings of the evolved sulphur dioxide.

Mercuric cyanide when boiled evolves traces of hydrocyanic acid, but no mercury, even when concentrated. When, however, the point of saturation is reached, small quantities of mercury can be detected in the distillate; but if the evaporation to dryness is carried on without ebullition, as on a steam-bath, no mercury is volatilised. It will be seen from this, that, after estimating mercury by potassium cyanide, it may be evaporated to small bulk for estimation by the battery, without any loss whatever.

Experiments were made to find if mercurous or mercuric nitrate were volatile. Neither salt, when in dilute, or even moderately concentrated solutions, gives any mercury when distilled. When, however, the mercurous nitrate solution becomes concentrated, the distillate is sometimes of a slightly grey tinge.

When two or three drops of this solution are examined by the microscope, the grey substance is seen to consist of a flocculent matter like alumina, some very small shining pearly plates, and a few minute globules of metallic mercury. When dilute nitric acid is added to a solution of mercurous nitrate, and the mixture boiled, there is no mercury carried over, until the acid becomes sufficiently concentrated to oxidise the mercurous salt.

Whenever the evolution of the lower oxides of nitrogen begins, mercury can be detected in the distillate in sufficient quantity to give a black, nearly opaque liquid with stannous chloride. Whenever the oxidation ceases, no more mercury is found in the distillate, or only very faint traces in a concentrated acid solution. It is curious that on oxidising metallic mercury with nitric acid, no mercury comes over, although far more nitrous fumes are evolved than on oxidising a mercurous salt.

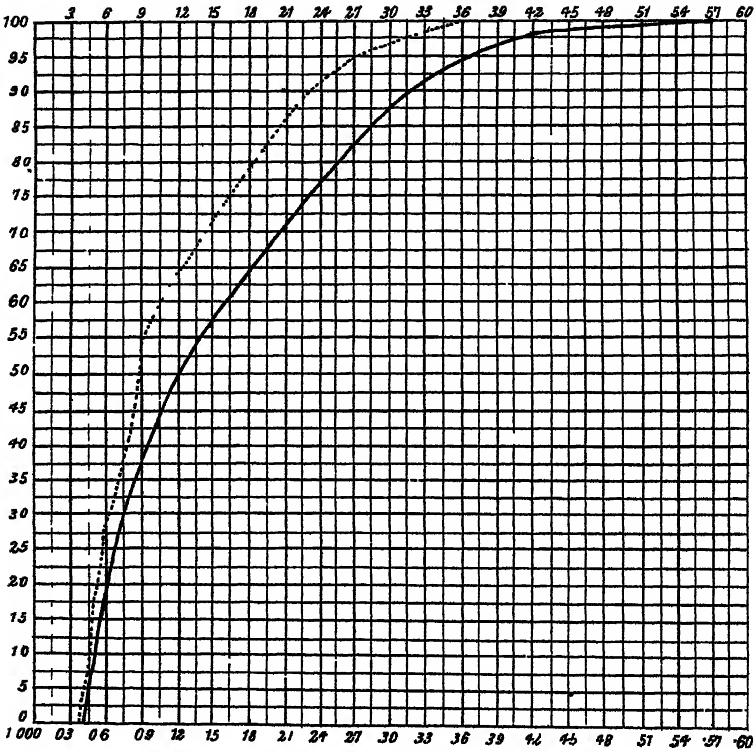
On finding how volatile mercuric chloride was, I thought it might be useful to determine the amounts of salt dissolved at different temperatures, as previous determinations had, in all probability, been made by evaporating a measured portion of the liquid to dryness. I also undertook the work as a test of the new volumetric process. In making the determinations, water kept at the desired temperature was digested on an excess of the carefully crystallised salt for at least half an hour, a portion was then drawn off with a bulb pipette kept at the same temperature, whose contents at 0° had been accurately determined. At 0° the amount dissolved was determined in two ways—first a solution saturated at about 15° was cooled down to 0° and allowed to stand at that temperature for an hour or so; the amount dissolved was then determined. The second method was to cool down water to 0° and then add an excess of the crystallised salt. The two methods gave closely agreeing results, the former being generally a little higher than the latter. When a saturated solution, from 97·5° upwards, is sucked up into a bulb, the salt invariably crystallises and blocks up the capillary point whenever the bulb is removed from the solution, so that, in determining the amount dissolved from 97·5° to 100·8° (the boiling-point of a saturated solution of mercuric chloride), the following process was employed:—The small dry bulb (whose contents at 0° were known) was plunged under the solution, and allowed to remain there till the liquid rose to the mark on the neck. The upper tube was then sealed, the bulb removed from the solution, and the outside wiped quite clean. The capillary tubes were then broken off at each end, the bulb broken in a beaker, and the salt dissolved in cold water. The small tubes were then ground in an agate mortar, and the mixture of glass and salt washed into the beaker. The whole of the salt being in solution in the beaker, it was only necessary to add a few drops of

ammonia, and estimate by standard cyanide solution. The following table gives the results of amounts dissolved and densities. The determinations were made almost without exception at each rise of 5°, and at each end, some intermediate ones were made. The densities were determined in the usual way, with a fine blown bulb, whose contents at 0° were accurately known.

Temperature.	Per cent. dissolved.	Specific gravity.	Temperature.	Per cent. dissolved.	Specific gravity.
0·0°	4·09	1·039	60°	16·23	1·116
2·2°	4·35	1·039	65°	18 42	1·124
4°	4 61	1·039	70°	20·81	1·116
5°	4·78	1·041	75°	22 70	1·165
10°	4 85	1·042	80°	26·52	1·181
15°	5·59	1·045	85°	28·74	1·203
20°	5·93	1·049	90°	32·30	1·225
25°	6·68	1·056	95°	36·71	1·272
30°	7·17	1·060	96·5°	37·82	1·287
35°	8·86	1·067	97·5°	41·56	1·310
40°	9·72	1·076	99°	52·51	1·346
45°	10·61	1·083	100°	55·73	1 354
50°	12·37	1·089	100·8°	56·02	1·357

The curves in the accompanying illustration are constructed from the above numbers, the continuous line referring to the amount dissolved, and the dotted line to the densities. The lateral numbers refer to the temperature, the upper to the percentage of salt dissolved, and the lower to the specific gravity.

In conclusion, I may mention that of the two processes the volumetric one is both more accurate and easier of application. It might be expected that the platinum basin used in the battery estimations would be seriously acted upon, but on dissolving off the mercury by nitric acid, the surface of the basin remains bright and clear, showing that the amalgamation is extremely superficial. The basin lost 8 milligrams in ten estimations, showing a loss of eight-tenths of a milligram for each estimation, which is not much more than would be caused by cleaning it. The loss depends entirely on the nature of the basin, some specimens of platinum being much more easily amalgamated than others.



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XXIV.—*Note on a Reaction of the Acetates upon Lead Salts, with Remarks upon the Solubility of Lead Chloride.*

By Frederick Field, F.R.S.

When sodium chloride is added to either acetate or nitrate of lead, if the solutions be sufficiently concentrated, it is well known that a white precipitate is formed, and this is regarded as lead chloride. But chemists are perhaps not generally aware of the fact that if acetic acid be immediately added to the precipitate produced in the acetate solution, the whole is entirely dissolved for the moment, but crystals of lead chloride speedily begin to form; the precipitate in the lead nitrate solution remains unchanged on the addition of acetic acid. And further, if to the clear solution, after the precipitation of lead nitrate by sodium chloride, any acetate be added, even in the cold, a cloudiness is immediately formed which gradually becomes a precipitate. This is particularly the case with copper acetate, which, if agitated with the solution above referred to, yields in a few hours a copious deposit, perfectly soluble in acetic acid. It was thought at first that this might prove a characteristic test for the acetates, but experience showed that the formates and probably other members of that group yielded the same reaction. It occurred to me subsequently that it might be the insolubility of the acetates in sodium chloride that produced these somewhat singular results, and although experiments did not show that this was entirely the case, it sufficiently proved that sodium chloride took an important part in the reaction, as copper acetate gives a precipitate in strong solution of sodium chloride. This does not happen with ammonium, sodium, or potassium acetate, yet if one drop of a lead salt be added, a precipitate is produced which is immediately soluble in acetic acid. Formates and acetates can thus be easily distinguished from malates, tartrates, citrates, phosphates, &c., the soluble salts of which yield precipitates with lead solutions, but are *insoluble* in acetic acid. But by far the most sensitive test for the presence of acetates and formates is the employment of a copper salt. When copper acetate is largely diluted with water and boiled, the greater part is decomposed; free acetic acid is evolved, and black copper oxide precipitated, but even long-continued ebullition fails to effect entire decomposition. When, however, one-thousandth part of copper acetate is merely heated with sodium chloride, an immediate precipitate is produced, with formation of oxychloride of copper, which does not blacken or change colour after prolonged boiling. It is, of course, unnecessary to use this copper acetate. If a drop of any acetate be added to copper nitrate or chloride, and gently warmed,

especially in the presence of sodium chloride, the reaction is very evident. Although it has been stated that formates and acetates behave similarly, an experienced eye can detect the difference. Formic acid gives a blackish-grey deposit, evidently containing free oxide of copper, whilst acetic acid yields a bright grass-green precipitate unchanged by any duration of ebullition.

Mr. Carter Bell, in an elaborate and interesting paper (*Chem. Soc. Journal*, xxi, 350) on the Solubility of Lead Chloride, states the remarkable fact that this salt becomes less soluble when hydrochloric is added to a certain point, and increases in solubility when more of the acid is added. Pure water dissolves 0 946 or 1 in 120; with the addition of 1 per cent. hydrochloric acid, only 0 347, while with 14 p.c. of the acid 0·090 is dissolved, which is the maximum quantity. After the liquid becomes more acidified, the solubility of the salt increases, so that at 72 per cent. of acid it is more soluble than in water, and in the pure acid (sp. gr. 1·162) as much as 2·900 is dissolved. The reaction is rather different when sodium chloride is used as a solvent. My own experiments proved that the solubility of lead chloride in pure water was 1 part in 120, agreeing exactly with the result obtained by Mr. Bell. On the addition of sodium chloride to the extent of 5 per cent., its solubility decreased very considerably, and only 1 in 437 remained in solution. When, however, the lead salt was digested with a concentrated solution of sodium chloride, it was found to be rather less soluble than in water, viz., 1 in 129. This fact can be exemplified in an interesting manner by the addition of solution of sodium chloride to an aqueous solution of lead chloride, when crystals of the latter are deposited, and *vice versâ*, when water is added to a solution of lead chloride in concentrated sodium chloride.

Although chemists are aware that when lead sulphate is treated with hydrochloric acid, lead chloride is formed and free sulphuric acid remains in solution, it may probably not be known how immediately even a cold saturated solution of sodium chloride decomposes lead sulphate. And it almost appears that at first there is not only an actual decomposition, but a solution, as 1 gram of lead sulphate dissolves perfectly in 100 grams of solution of sodium chloride, and after some hours deposits crystals of lead chloride. Sulphuric acid, or a soluble sulphate gives no precipitate with lead chloride dissolved in sodium chloride. Mr. Bell has also remarked upon the different forms of crystals of lead chloride, some being in fine needles and others in feathery plates. Both varieties can be obtained most beautifully by the following method. A solution of aniline hydrochloride forms lead chloride with difficulty; indeed both solutions must be rather concentrated before any reaction is perceptible. On leaving the liquid to stand some time, fine needle-shaped crystals are deposited, and if to the

mother-liquor a few drops of sodium chloride be added, a beautiful mass of iridescent scales is produced, differing entirely in physical structure from the former. An observation of no great importance may also be mentioned. When potassium iodide is added to a solution of lead chloride in sodium chloride, the precipitate is not amorphous, but has the brilliant spangly appearance which it presents when deposited from its solution in hot water.

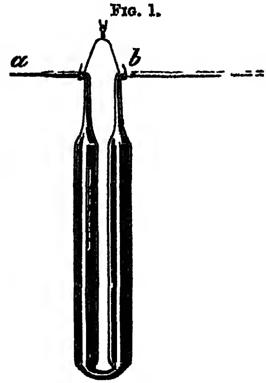
It may be mentioned in conclusion that the most sensitive test for the presence of an acetate or formate is a solution of copper chloride in sodium chloride. When this is gently warmed and remains perfectly bright a very minute amount of either a formate or acetate yields a precipitate; but it may be advisable to add a trace of lead salt and boil, as the phosphates, &c., of copper are more soluble in acetic acid than the corresponding lead salts.

XXV.—*A Method of Determining the Specific Gravity of Liquids with Ease and Great Exactness.*

By HERMANN SPRENGEL, Dr. phil.

THE *Laboratory* for 1867 (p. 191) contains a paper on Specific Gravity, by Matthiesen and Hockin, in which the use of a small pipette is recommended in place of the specific-gravity bottle, when only a few centigrams of liquid are at the operator's disposal. I also had independently, for a number of years, availed myself under all circumstances of pipette-shaped vessels in preference to the usual specific-gravity bottle. But our instruments, and our way of using them, differ sufficiently to justify me in giving a short description of my method.

FIG. 1.

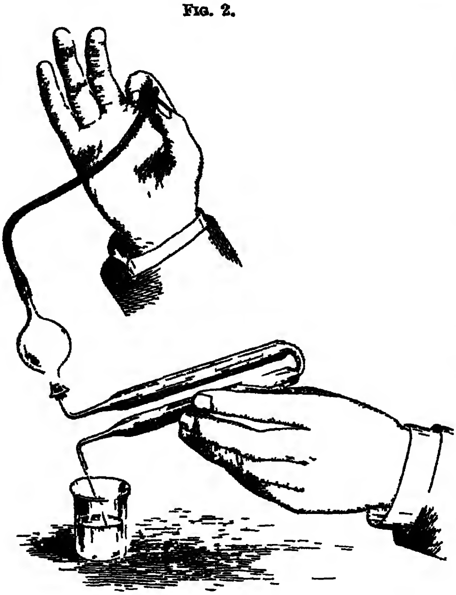


The form of my instrument, as shown in Figure 1, is that of an elongated U-tube, the open ends of which terminate in two capillary tubes, which are bent at right angles in opposite directions. The size and weight of this instrument should be adapted to the size and capability of the balance, in which it is to be weighed. As our usual balances indicate $\frac{1}{10}$ milligram when loaded with 50 grams, the U-tube, when charged with the liquid, should not be heavier (1000 grains = 64,799 grams). The instrument which served for my determinations, mentioned below, had a

length of 17·7 cm. (7 inches), and was made of a glass tube, the outer diameter of which was 11 mm. ($\frac{7}{16}$ of an inch). It hardly need be mentioned that the U-shape is adopted for the sake of presenting a large surface, and so rendering the instrument sensitive to changes of temperature. The point, however, which I wish to notice more particularly (for reasons explained below) is the different calibre of the two capillary tubes. The shorter one is a good deal narrower (at least towards the end) than the longer one, the inner diameter of which is about $\frac{1}{2}$ mm. The horizontal part of this wider tube is marked *near* the bend with a delicate line (*b*). This line and the extremity of the opposite capillary tube (*a*) are the marks which limit the volume of the liquid to be weighed.

The filling of the instrument is easily effected by suction, provided that the little bulb apparatus (as represented in Figure 2) has previously been attached to the *narrow* capillary tube by means of a perforated stopper, *i.e.* a bit of an india-rubber tube, tightly fitting the conical tubulus of the bulb. On dipping the *wider* and longer capillary tube into a liquid, suction applied to the open end of the india-rubber tube will produce a partial vacuum in the apparatus, causing the liquid to enter the U-tube. As this partial vacuum maintains itself for some time (on account of the bulb, which acts as an air-chamber), it is not necessary to continue the suction, if the end of the india-rubber tube be timely closed by compression between the fingers. When bulb and U-tube have about equal capacity, it is hardly necessary during the filling to repeat the exhaustion more than once. Without such a bulb, the filling of the U-tube through these fine capillary tubes is found somewhat tiresome. The emptying of the U-tube is effected by reversing the action and so compressing the air.

FIG. 2.



After the U-tube has been filled it is detached from the bulb, placed in water of the standard temperature almost up to the bends in the

capillary tubes, left there until it has assumed this temperature, and, after a careful adjustment of the volume, it is taken out, dried, and weighed.

Particular care must be taken to ensure the correctness of the standard temperature, for (as I shall show below) a mistake of 0·1° causes the weight of 10 c.c. of water to be estimated either too high or too low by 0·14 milligram, giving rise to an error in the 5th decimal, or making 100000 parts 100001·4 parts. Those determinations have been made in Dupré's* apparatus, which, when furnished with a sensitive thermometer, allows the fluctuations of temperature to be fixed within the limits of 0·01°. If many determinations had to be made I should avail myself of Scheibler's (*Zeitschrift für analytische Chemie*, vol. vii, p. 88, 1868) electro-magnetic regulator for maintaining a constant temperature.

A peculiar feature of my instrument is the ease and precision with which the measurement of the liquid can be adjusted at the moment it has taken the standard temperature; for it will be found that the liquid expands and contracts only in the wider capillary tube, viz., in the direction of the least resistance. The narrow capillary tube remains always completely filled. Supposing the liquid reaches beyond the mark *b*, it may be reduced through capillary force by touching the point *a* with a little roll of filter-paper. Supposing, however, that in so doing too much liquid is abstracted, capillary force will redress the fault, if point *a* be touched with a drop of the liquid under examination; for this gentle force acts instantly through the whole mass of the liquid, causing it to move forward again to or beyond the mark.

As the instrument itself possesses the properties of a delicate thermometer, the time when it has reached the standard temperature of the bath may be learned from the stability of the thread of liquid inside the wider capillary tube. The length of this thread remains constant after the lapse of about *five minutes*.

In wiping the instrument (after its removal from the bath) care should be taken not to touch point *a*, as capillarity might extract some of the liquid; otherwise the handling of the instrument requires no especial precaution.

The capillary tubes need not be closed for the purpose of arresting evaporation, at least that of water. I have learned from the mean of several determinations that the error arising from this source amounts in one hour to $\frac{1}{20}$ milligram.

In cases where the temperature of the balance-room is high and the expansion-coefficient of the liquid to be examined is considerable, it may be found necessary to put a small cap (bead-shaped and open at both

* A. Dupré and F. T. M. Page "On the Specific Heat," &c. (*Phil. Trans.* 1869, p. 608).

ends) over the extremity of the *wider* capillary tube, for the purpose of retaining the liquid, which during the time of weighing might otherwise be lost, owing to its expansion. Raising the standard temperature of the bath is another way of meeting this inconvenience. When a cap is used, the wider capillary tube need not be longer than the narrow one.*

The nicety attainable by this method is very satisfactory. As a proof of this I beg to draw attention to the following two examples:—

1. Six weighings in succession were made of the same sample of distilled water, measured three times at 16°, three times at 15°. The instrument was filled and emptied three times, while Dupré's bath was raised and lowered to the desired temperature six times in succession. The weighings were noted down after the instrument had hung inside the balance-case for ten minutes. No counterpoise was used in the shape of another similar U-tube. The results were these:—

		At 16°.		At 15°.
U-tube + water..	=	41·9648 gram.		41·9675 gram.
U-tube..........	=	23·3332 „		23·3332 „
		18·6316 gram.	:	18·6343 gram.
Specific gravity		1	:	1·000145
		At 16°.		At 15°.
U-tube + water..	=	41·9648 gram.		41·96745 gram.
U-tube..........	=	23·3332 „		23·33320 „
		18·6316 gram.	:	18·63425 gram.
Specific gravity		1	:	1·000143
		At 16°.		At 15°.
U-tube + water..	=	41·9648 gram.		41·9674 gram.
U-tube..........	=	23·3332 „		23·3332 „
		18·6316 gram.	:	18·6342 gram.
Specific gravity		1	:	1·000140

NOTE.—This table shows that the instrument is obviously applicable also to the exact determination of the apparent expansion-coefficient of liquids.

2. A sample of water taken from the Houses of Parliament on the 29th of March, 1873, as supplied by the Government Water Works near Trafalgar Square from an Artesian well 380 feet deep, showed at 15° .... 1·000794 sp. gr.
while, after being boiled for ¾ hour under the usual precautions, it showed .... 1·000711 „

Difference .... 0·000083

* The instrument may be obtained from E. Cetti and Co., 11, Brooke Street, Holborn, London.

On evaporating 100 grams of the water (unboiled), the solid residue was found to weigh	0·0835 gram,
while the solid residue from 100 grams of water (boiled and filtered) weighed	0·0775 „
Difference	0·0060 gram.

This water, although it contains a considerable amount of mineral matter, was chosen on account of its softness, for, by Clark's test, its

degree of hardness (unboiled) was	5·3
(boiled)	0·75
Difference	4·55

These data suffice to prove that the well known precipitation of carbonate of lime through boiling (in this case 4·55 grains per gallon) was the main cause of lowering the specific gravity of the water after boiling. As we have learned from example No. 1 that reliance may be placed on the correctness of the 5th decimal, the quantity of matter (with reference to the above difference 0·000083) which became insoluble might have been eight times less before its absence ceased to be indicated by such specific gravity determinations. Now the 8th part of 0·006 gram is 0·00075 gram, and represents the difference which refers to the solid residue from 100 grams of water. In other words, if we dissolve in 10,000,000 parts 75 parts, or in 1 litre of water 7·5 milligrams, or in 1 gallon about $\frac{1}{2}$ grain of mineral matter (such as carbonate of lime), its presence in the water can thus be ascertained quantitatively.

If the varying constituents dissolved in natural waters influenced the specific gravity of water to a like degree, the above method would give the readiest means for determining the amount of matter in solution, but an approximation only can thus be obtained.

When, however, a solution contains only one unknown constituent, the relative proportion between this constituent and its solvent, can by means of this simple and quick analytical operation, be ascertained with all the accuracy needed.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Modifications of the Spectrum of Chlorophyll under the Influence of Alkalis. By J. Chautard (Compt. rend., lxxvi, 570—572).

An alcoholic solution of chlorophyll mixed with a few drops of solution of caustic potash or ammonia is very little changed. But by boiling with solution of caustic potash, the characteristic absorption band in the red is divided into two, whilst the rest of the chlorophyll bands disappear almost entirely. These two bands reunite on acidifying the liquid with acetic acid, and may be again separated by adding ammonia.

W. A. T.

On an Air Battery. By J. H. Gladstone and Alfred Tribe (Proc. Roy. Soc., vol. xxi, 247).

It was shown by the authors (*Proc. Roy. Soc.*, vol. xx, 290) that when pieces of copper and silver, touching or connected by a wire, are immersed in an aërated solution of pure copper nitrate, a decomposition of the salt ensues accompanied by a deposition of cuprous oxide on the silver, with a corresponding solution of the copper, and a flow of electricity through the liquid from the positive to the negative metal.

The following formulæ may render the reaction intelligible:—

Before contact—

$$m\text{Ag} + \text{O} + \text{Cu}2\text{NO}_3 + \text{Cu}2\text{NO}_3 + n\text{Cu};$$

After contact—

$$m\text{Ag} + \text{Cu}_2\text{O} + \text{Cu}2\text{NO}_3 + \text{Cu}2\text{NO}_3 + (n—2)\text{Cu}.$$

The authors showed, moreover, that this decomposition takes place only when the oxygenised solution of copper nitrate is in contact with the silver, and that it is independent of any action of free oxygen on the copper.

It seemed of interest to examine, more fully, the electrical side of this reaction: hence the present communication.

It will be apparent that if free oxygen could be supplied to the solution at the same rate as it combines to form cuprous oxide, the action would go on at about the same rate as long as any metallic copper remained.

To facilitate this as much as possible, the authors arrange that the silver plate shall have a horizontal position just under the surface of the liquid in the cell; and, in fact, they convert it into a small silver tray full of crystals of the same metal, which rise in projections above the surface. The copper plate lies horizontally under it, separated, if need be, by a piece of muslin, and connection is made by a wire as usual. Holes are made in the silver tray with the view of facilitating the movements of the salt in solution. The solution itself may be contained in a shallow trough or saucer, and the whole arrangement put upon a wooden stand, the plates being attached to two uprights fixed in the stand.

The best proportionate areas of the silver and copper plates were investigated. It thus appeared that an increase in area of the silver plates causes almost a proportionate increase in the current. It was also found that heat greatly increases the activity of this cell, a cell giving a deflection of 40 at 20° C., gave one of 250 at 50° C.; and the increase in the higher degrees of this range of temperature was much greater than in the lower.

The strength of copper nitrate which gives about the maximum effect is 6 per cent.

From the nature of the reaction it might be expected that the current would gradually diminish on account of the using up of the oxygen in the neighbourhood of the silver. Such a diminution always does take place at first—agitating the liquid ought, under these circumstances, to increase the action. It does so.

It might also be expected that upon breaking contact for some time, so as to allow of the absorption of oxygen from the air, the current upon again making contact would be as strong, or nearly so, as originally. This also was found to be the case.

An experiment was made by putting a cell, with plates connected by a wire, under a bell-jar full of air over mercury. It was expected that the mercury would rise inside the jar from absorption of the oxygen. The mercury did rise, and the oxygen was so completely removed that a lighted taper was immediately extinguished in the remaining gas.

Comparative experiments were made with aërated and deaërated solution of copper nitrate. It was found that the amount of action in the latter case was small and clearly attributable to the difficulty of completely excluding air.

Two experiments were made alike in all respects, except that in one case the cell used was filled with a solution simply deprived of oxygen, while the other cell was filled with a solution through which a current of CO_2 had been passed for some time. The first was placed in the air, and gave a deflection of 110 rising to 115, but the second was placed in a vessel full of carbonic acid gas, and gave a deflection of 20, which gradually fell to three.

It was proved experimentally that the cuprous oxide deposited on the silver was compensated by an equivalent solution of the copper plate. The cuprous oxide is sometimes deposited in crystals visible to the naked eye, and shown by a lens to be regular octohedrons.

One cell having plates two inches in diameter was found sufficient

to decompose such metallic salts as the nitrates of copper, silver, and lead, platinum being used for the negative electrode, and for the positive the same metal as existed in the salt experimented on. Six cells were sufficient to decompose dilute sulphuric acid, and dilute hydrochloric acid pretty quickly, copper electrodes being employed.

The theoretical interest of this battery lies in the fact that it differs from all other galvanic arrangements, inasmuch as the binary compound in solution is incapable of being decomposed either by the positive metal alone or by the two metals in conjunction, without the presence of another body ready to combine with one of its elements when set free."

Grove's gas battery is essentially different from this, if the oxygen and hydrogen condensed on the platinum plates play the part of the two metals; but it closely resembles this if hydrogen acts the part of the positive metal, and platinum that of the negative; the dilute sulphuric acid will then be decomposed on account of the simultaneous presence of the oxygen which can combine with the liberated hydrogen. Viewed in this manner, Grove's gas-battery is only a special case of the reaction mentioned in the communication to the Royal Society, and the formulæ will be :—

Before contact—

$$m\mathrm{Pt} \mid \mathrm{O} \mid \mathrm{H_2SO_4} \mid n\mathrm{H}.$$

After contact—

$$m\mathrm{Pt} \mid \mathrm{H_2O} \mid \mathrm{H_2SO_4} \mid (n-2)\mathrm{H}.$$

The practical interest of this arrangement lies in the fact that it is an approximation towards a constant air-battery. Should it ever come into use elsewhere than on the lecture table, it will probably be in the form of a combination of zinc and copper, with an aërated solution of zinc chloride: for that arrangement has an electromotive force equal to six times that of the arrangement we have more particularly studied, and about three-quarters that of a Daniell's cell.

A. T.

Contributions to Crystallography. By C. KLEIN (Ann. Chem. Pharm., clxvi, 179—200).

(1.) *Benzhydroxamic acid*, $NH_2(C_7H_5O)O$. Rhombic, $\breve{a} : \bar{b} : \dot{c} =$ 0·325563 : 1 : 0·321707. Observed forms: ∞P, $\infty \breve{P} \infty$, $\breve{P} \infty$, $\bar{P} \infty$. Cleavage, perfect parallel to $\infty \breve{P} \infty$.

Optical relations: Plane of optic axes = *b c*. Acute, positive median line perpendicular to $\infty \breve{P} \infty$. Strong double refraction. Dispersion = 0. 2E (mean value for white light) = 50° $2\frac{1}{2}'$.

(2.) *Dibenzhydroxamic acid*, $NH(C_7H_5O)_2O$. Rhombic, $\breve{a} : \bar{b} : \dot{c} =$ 0·671972 : 1 : 0·319461. Observed forms: 0P, $\infty \breve{P} \infty$, $\infty \bar{P} \infty$, ∞P, $\breve{P} \infty$, $2\breve{P} \infty$, $\bar{P} \infty$, $2\bar{P} \infty$. Cleavage, perfect parallel to ∞P.

Plane of optic axes = *b c*. Acute positive median line perpendicular to $\infty \breve{P} \infty$. Strong double refraction. Dispersion $\rho < v$; 2E (mean) = 54° 35′ for red, 56° 22′ for blue light.

(3.) *Tribenzhydroxylamine*, $N(C_7H_5O)_3O$. Crystals very small, but well defined and transparent.

Monoclinic: $\grave{a} : \bar{b} : \acute{c} = 1 : 1\cdot115835 : 0\cdot334900$; $L = 83° 21' 20''$. Fundamental angles: $-P : -P = 149° 24'$; $\infty P : \infty P = 96° 36'$; $-P : \infty P = 118° 14'$. Observed forms: ∞P, $-P$, $\mathrm{P}\infty$, $\infty P\infty$, $\infty \mathrm{P}\infty$. The first three forms are well defined and lustrous; the rarer forms, $\infty \mathrm{P}\infty$ and $\infty P \infty$, are striated, often also curved. The character of the crystals is prismatic in the direction of ∞P; they cleave perfectly parallel to $\infty P \infty$.

The plane of the optic axes is $a\ c$, that is to say, identical with the plane of symmetry. The acute positive median lines for the different colours are nearly at right angles to the plane $\infty P \infty$ in which the crystals cleave. Such a cleavage fragment, when viewed in air, shows one optic axis at the edge of the field of view; in oil, two axial figures are visible. The double refraction is strong. Dispersion $\rho < v$.

(4.) *Benzamide*, $NH_2(C_7H_5O)$.—Monoclinic, $\grave{a} : \bar{b} : \acute{c} = 1 : 0\cdot228404 : 1\cdot016827$; $L = 89° 22'$. Fundamental angles, $0P : \infty P \infty = 90° 38'$; $+P\infty : \infty P \infty = 135° 10'$; $\infty P : \infty P = 154° 16'$ in the orthodiagonal principal section. Observed forms: ∞P, $\infty P \infty$, $0P$, $+P\infty$, $+\frac{1}{2}P\infty$.—The crystals obtained by fusion are almost always twins, whose twin-axis is the principal axis, and face of combination $\infty P \infty$. A solution of benzamide in ether often yields simple crystals together with twins; an alcoholic solution for the most part, only simple crystals. The crystals are sometimes prismatic, elongated in the direction of ∞P; sometimes they have also short prismatic forms. Occasionally they are tabular parallel to $\infty P \infty$, and lengthened in the direction of the orthodiagonal. They cleave perfectly parallel to $\infty P \infty$, less easily parallel to $+P\infty$. The faces ∞P and $\infty P \infty$ have a strong lustre; $0P$, $P\infty$, and $+\frac{1}{2}P\infty$ are more or less striated. The crystals are colourless, seldom quite transparent.

The plane of the optic axes coincides with the clinodiagonal principal section. The two principal directions of vibration are so situated in this plane that one runs nearly parallel to $P\infty$, the other nearly at right angles to it. The first of these directions is inclined to $\infty P \infty$ at the angles $49° 53'$ and $130° 7'$, the obtuse angle being turned towards $0P$. Dispersion $\rho < v$. $2H = 100° 15'$ red; $102° 10'$ blue.

(5.) *Luteocobaltic Chloride*, $Co_2Cl_6.12NH_3$.—Monoclinic, $\grave{a} : \bar{b} : \acute{c} = 1 : 1\cdot7115941 : 1\cdot1128766$; $L = 57° 31' 9''$. Fundamental angles: $0P : +P\infty = 113° 12'$; $+P : +P\infty = 151° 45'$; $\infty P : \infty P = 127° 30'$. Observed forms: $0P$, $+P\infty$, $+2P\infty$, $+P$, $2\mathrm{P}\infty$, $\infty\mathrm{P}\infty$, ∞P, $\infty\mathrm{P}3$; more rarely $+\frac{1}{2}P$, $\infty P \infty$; as twin-face, $+\frac{1}{2}P\infty$. The character of the crystals is sometimes tabular according to $0P$, sometimes prismatic according to ∞P, in the latter case with felspathic development.

The crystals seldom occur as simple individuals, but frequently as aggregates, some of which may be referred to regular, so-called twin-combinations, in which either (1), the twin-axis is the principal axis, and combination face $\infty P \infty$; or (2), the twin-axis is normal to $+\frac{1}{2}P\infty$; twin and combination-face $+\frac{1}{2}P\infty$. The combinations formed according to the first law are contact-twins always implanted by the end which exhibits the re-entering dome-angles; those formed

according to the second law are either contact or intersecting twins. Besides these regular combinations, others frequently occur which are formed with a certain regularity, but cannot perhaps be called twin-crystals in the ordinary sense of the word. Their structure may be understood by regarding them as formed according to the following law:—Twin-axis normal to the base; combination- and twin-plane, the base; angle of rotation 180°.

The plane of the optic axes is perpendicular to the plane of symmetry, and the first positive median line is nearly at right angles to 0P, while the second coincides with the orthodiagonal.

The crystals of luteocobaltic chloride were previously measured by Dana,* and referred by him to the rhombic system. Klein discusses these measurements, and comes to the conclusion that the crystals, from their symmetry, angular relations, modes of twin-formation, and optical properties, really belong to the monoclinic system.

(6.) *Isuretine*, CH_4N_2O.—The crystals of this isomeride of urea have very smooth faces, which reflect moderately well, but after a few minutes' exposure to the air, become dull, from absorption of moisture, and the previously sharp edges begin to melt off. The angular measurements are therefore attended with considerable difficulty.

The crystals belong to the rhombic system, $\breve{a} : \bar{b} : \hat{c} = 0{\cdot}65563 : 1 : 1{\cdot}12041$. Fundamental angles: $\infty P : \infty P = 113° \ 30'$; $\breve{P}\infty : \breve{P}\infty = 83° \ 30'$. Observed faces: ∞P, $\breve{P}\infty$, $1\frac{P}{2}$, more rarely 0P, still more rarely $r\frac{P}{2}$. Character prismatic in the direction of ∞P. Colour white; only the small crystals are perfectly transparent. No distinct cleavage perceptible.

The plane of the optic axes is $a\ b$. The first positive median line is at right angles to the perpendicular truncation of the acute lateral edge, and therefore coincides with b. Dispersion $\rho < v$.

Very remarkable is the occurrence in this body of the rhombic sphenoïd, $1\frac{P}{2}$, which is much more frequently developed than its correlative, $r\frac{P}{2}$. Here indeed it is impossible to overlook a certain tendency to hemihedral formation, which is common to the two isomeric bodies, urea and isuretine; in the former, as is well known, the quadratic primary pyramid likewise occurs as a sphenoid.

The original memoir contains numerous angular measurements of the crystals above described, and is accompanied by figures.

H. W.

* [Res]earches on the Ammonia-cobalt Bases, by Gibbs and Genth, 1856, p. 45.

On the Apparent Variability of Dulong and Petit's Law.

By M. HIRN (Compt. rend., lxxvi, 191—194).

THE apparent deviations from Dulong and Petit's law, which have lately induced some physicists to raise doubts as to its general validity, are shown to be due to a wrong definition of specific heat. If q = total heat communicated to a body, A = mechanical equivalent of heat, k = *real* specific heat, e = external work performed by the expanding body, i = internal work done against molecular forces, cohesion, etc., and t_0 and t_1 = the initial and final temperatures of the body, then

$$q = k\,(t_0 - t_1) + Ae + Ai.$$

The ratio $\frac{q}{t_0 - t_1}$ was taken by Dulong and Petit as the measure of specific heat, and is often spoken of as such, even now, *instead of the quantity* k, *i.e., the quantity of heat which actually contributes to the rise of temperature.*

The value of $\frac{q}{t_0 - t_1}$ varies with the value of $A(e + i)$ which may depend upon the temperature or upon the state of aggregation of the body; it cannot therefore be expected to be constant. If, nevertheless, with twenty elementary substances, solid or liquid, it is found to be nearly constant, we must, as in this case e may evidently be neglected, conclude that i, the internal work, is a function of the atomic weight.

With solids and liquids we have no means of determining i, and therefore cannot obtain the value of k, or the true specific heat.

In the case of the three gases, hydrogen, oxygen, and nitrogen, we know the internal work to be exceedingly small, and, as we can measure the external work e by their expansion, we have all the required data for the determination of k, which is found to be invariable and absolutely identical. Thus Dulong and Petit's law holds good in those cases where it can fairly be tested, and we may infer that we should find it to be universally true if, by the specific heat of a body, we understood the total heat communicated to it *minus* that spent upon external and internal work.

R. S.

Synaphy of some Substances hitherto uninvestigated, especially the Compound Ethers.

By R. SCHOLZ (Pogg. Ann., clxviii, 62—76).

As the terms cohesion and adhesion have had various meanings assigned to them, Frankenheim (*Die Lehre von der Cohasion*, Breslau), proposed the term "*synaphie*" to indicate the attractive force which holds together the homogeneous parts of a fluid, and that of "*prosaphie*," for the attraction which exists between fluids and solid bodies. After remarking that liquids, in their behaviour towards solid bodies, may be divided into two classes, namely, those which wet them and those which do not, and that their synaphy can be measured either by means

of adhesion plates or by capillarity, the author gives a summary of the results of the observations which have hitherto been made on the cohesion and adhesion of liquid bodies, especially noticing the influence of temperature.

Considered with respect to this property, liquids may be divided into three classes, the first of which includes only water, which has the highest synaphy of any known liquid; the second, compounds of organic and inorganic substances with water; and the third, anhydrous substances, such as alcohol, ether, rock-oil, carbon sulphide, and certain volatile oils; these are found to possess the lowest specific synaphy.

The second part of the paper contains the author's own observations made with circular adhesion plates of the following materials: polished glass, ground glass, copper, brass, zinc, and mahogany; also with capillary tubes of ·98992 mm., ·89452 mm., and ·22298 mm. radius respectively.

Amongst the seventeen substances examined were ethylic oxide, nitrate, acetate, butyrate, and formate, potassium ferrocyanide and ferricyanide, ammonium chloride and sulphide, barium acetate, and water. Of these, water possesses the greatest synaphy and ether the least; the synaphy of all the compound ethers is also very low when compared with other liquids. The formula, $M = \frac{p}{mr^2\pi} = \frac{\rho}{m}\sqrt{2sd}$, expresses the absolute synaphy of a given liquid, that is, the weight necessary to separate the adhesion plate reckoned in millionths of an atmosphere; p = weight necessary to separate a circular adhesion plate whose radius is r from the liquid; m = the pressure of one atmosphere on a square millimeter = 10301 milligrams; ρ = density of the liquid; and d the capillary height in a tube whose radius is s millimeters.

A table accompanies the memoir, giving the values of M and M : ρ for each of the substances examined as deduced from the experiments with adhesion plates and with capillary tubes. As water between 0° and 4° presents an exception to the general law of expansion of liquids under the influence of heat, so does it present a similar exception with respect to its synaphy within this range of temperature.

C. E. G.

On Double Decomposition in Absence of Water.

By G. Gustavson (Deut. Chem. Ges. Ber., v, 1101).

Carbon tetrachloride and tetrabromide are not decomposed by water, and consequently if they are mixed with the chlorides and bromides $ROCl_3$, $ROBr_3$, BCl_3, BBr_3, $SiCl_4$, &c., the quantity of these compounds can be readily ascertained by decomposing the product of the reaction with water and precipitating the solution with silver nitrate. It appears that the direction in which the reaction goes on depends chiefly on the atomic weights, inasmuch as compounds of elements

having a similar atomic weight are formed. Further details will be given in a future communication.

C. S.

Researches on Saline Decompositions. By L. Joulin (Compt. rend., lxxvi, 558—562).

It is a well-established fact that when a solution of alkaline carbonate is mixed with a solution of certain metallic salts, there is precipitated, according to circumstances, either a pure carbonate, a hydrocarbonate, or a hydrate. The author has investigated the circumstances under which such double decomposition takes place.

Observations were made with the salts of manganese, silver, copper, and mercury; the details of the results obtained with manganese salts are regarded as typical. With equivalent quantities of manganese salt and alkaline carbonate, and at the ordinary temperature, the precipitate consists of pure manganese carbonate, and this is the case up to a dilution of $\frac{1}{200}$. Beyond this point, a mixture of carbonate and hydrate in indefinite proportions, results, the quantity of the latter increasing with the dilution and the temperature.

In concentrated solutions an excess of metallic salt gives a pure carbonate, but an excess of alkaline carbonate, under any circumstances, produces hydrate; at zero, however, the quantity of hydrate produced is scarcely perceptible, even for an excess of 40 equivalents of sodium carbonate.

The rapidity with which the reaction takes place was measured by filtering the liquor and titrating the uncombined alkali with standard acid. With equivalent quantities of the salts dissolved in a small quantity of water, 94 per cent. of the sodium carbonate was combined in five minutes, but the quantity so combined diminished steadily with the dilution, and when the original strength was reduced to $\frac{1}{5000}$, only 11·97 per cent. of alkali entered into combination during that interval. The immediate reaction is considerably retarded by an excess of one of the salts, and this retardation persists about 24 hours for an excess of 50 to 75 equivalents; the previous addition of a quantity of sodium sulphate to the solution also slightly retards the immediate reaction.

J. W.

Physical Properties of Carbonic Anhydride. By G. Recknagel (Pogg. Ann., cxlv, 469—480).

In a previous paper the author had developed the equation—

$$(1.)\quad Pv = A_0(1 + at)(1 - \frac{B_t}{v}),$$

in which P, v, α, t have their usual meaning, and $B_t = A_0(1 + \alpha t)\frac{1}{4M_t} = \frac{V}{2}$, where M_t is the tension of the saturated vapour, and V is its

specific volume. This equation, the advantage of which consists in connecting the conditions of saturated and superheated vapour, loses its application for temperatures above 31°, since Andrews has proved that above 36° carbonic anhydride behaves like a permanent gas—a result previously arrived at by the author by calculation from Regnault's number of the vapour-tension of carbonic anhydride, inasmuch as he found that its density did not increase with increase of temperature. For various reasons the author compares how far his equation agrees with the experimental results even at temperatures above 31°, and he arrives at the conclusion that it is probable that the function B diminishes very slightly with increase of temperature.

He also points out that the deviation from Boyle's law, caused by condensation of a small quantity of vapour on the sides of the vessel, must necessarily diminish with increase of the density of the gas, as then the difference in density of the bulk of the gas and the condensed portion is reduced.

R. S.

Flames of Compressed Gases. By F. Benevides (Ann. Chim. Phys. [4], xxviii, 358—363).

By means of an apparatus contrived by himself, and described in a previous communication, the author has made some observations on the phenomena of compressed coal gas escaping in the form of a jet into the atmosphere. These observations can hardly lay claim to novelty.

E. D.

On the Reflection of Light from Transparent Bodies and from Metals. By G. Quincke (Pogg. Ann. cxlviii, 311—317).

On the Fluorescence of some Solid Hydrocarbons in Coal-tar and Petroleum Residues. By Henry Morton (Pogg. Ann. cxlviii, 292—298). The chief results have already been given in this volume (p. 225).

On Fractional Distillation. By J. C. Glashan (Phil. Mag. [4], xlv, 273—276). A mathematical treatment of Wanklyn's theory (p. 345).

On the Action of Solid Bodies on Gaseous Supersaturated Solutions. By C. Tomlinson (Phil. Mag. [4], xlvi, 276—283).

Barometer with Self-registering Apparatus. (Dingl. polyt. J., ccvii, 464).

Improved Form of Grove's Battery. By H. Yeates (Dingl. polyt. J., ccvii, 504).

The Physometer, a New Instrument for Determining Variable Volumes of Air and other Gases. By P. Harting (Pogg. Ann., cxlviii, 143, and 214—270).

On an Acoustic Pyrometer. By A. M. MAYER (Pogg. Ann., cxlviii, 287—292).

A New Thermometer for Deep Sea Observations. By J. L. W. DIETRICHSON (Pogg. Ann., cxlviii, 298—301).

On a Water Air-pump. By N. JAGN (Ann. Chem. Pharm., lxxvi, 208—212).

Inorganic Chemistry.

On the Systemization of Inorganic Chemistry. By L. MEYER (Deut. Chem. Ges. Ber., vi, 101—106).

FROM the results of his experimental researches, Thomsen concludes that iodic acid is either a bibasic acid containing one atom of iodine in the molecule, or more probably that it is quadribasic and consists of $H_4I_2O_6.3H_2O$. To explain its constitution he assumes that it contains *monad* iodine and *tetrad* oxygen. Lothar Meyer strongly objects to these views; he has already pointed out (*Die Modernen Theorien der Chemie, &c.*, 2nd edition) that the theory of quantivalence and the law of the linking of atoms have only been deduced from the composition of gaseous compounds, and that it is not admissible to employ them for explaining the chemical constitution of solids and liquids. Before we can use these theories for this purpose, they have to be modified considerably, and must be either enlarged or restricted. Why should oxygen be a tetrad and iodine, which forms the compounds ICl_3 and ICl_4, only a monad? From our present stand-point, it appears much more rational to explain the constitution of iodic acid from the chemical nature of iodine and not from that of oxygen. Mendelejeff has shown that the composition of the highest oxides and corresponding hydrates appears as a regular periodical function of the atomic weight, if the elements are arranged in the natural system or according to the numerical values of their atomic weights. The position of each element in this system is therefore a similar periodical function, the cause of which can only be looked for in the chemical nature of the element itself. Thus we have the following natural families:—

Si	P	S	Cl
Ti	V	Cr	Mn
—	As	Se	Br
Zr	Nb	Mo	—
Sn	Sb	Te	I
Pb	Ta	W	—

These elements form the following hydrates, corresponding to the highest oxides*:—

* These formulæ are not intended to express the molecular weight, which, in most cases, is quite unknown.

$H_4Si_2O_6$	$H_4P_2O_7$	$H_4S_2O_8$	$H_4Cl_2O_9$
$H_4Ti_2O_6$	$H_4V_2O_7$	$H_4Cr_2O_8$	$H_4Mn_2O_9$
——	$H_4As_2O_7$	$H_4Se_2O_8$	$H_4Br_2O_9$
$H_4Zr_2O_6$	$H_4Nb_2O_7$	$H_4Mo_2O_8$	——
$H_4Sn_2O_6$	$H_4Sb_2O_7$	$H_4Te_2O_8$	$H_4I_2O_9$
$H_4Pb_2O_6$	$H_4Ta_2O_7$	$H_4W_2O_8$	——
$H_2Si_2O_5$	$H_2P_2O_6$	$H_2S_2O_7$	$H_2Cl_2O_8$
$H_2Ti_2O_5$	$H_2V_2O_6$	$H_2Cr_2O_7$	$H_2Mn_2O_8$
——	$H_2As_2O_6$	$H_2Se_2O_7$	$H_2Br_2O_8$
$H_2Zr_2O_5$	$H_2Nb_2O_6$	$H_2Mo_2O_7$	——
$H_2Sn_2O_5$	$H_2Sb_2O_6$	$H_2Te_2O_7$	$H_2I_2O_8$
$H_2Pb_2O_5$	$H_2Ta_2O_6$	$H_2W_2O_7$	——

Although neither all these hydrates nor their corresponding salts are known, we have a sufficient number of facts proving that these compounds form true homologous series, iodic acid, $H_4I_2O_9$, and its salts belonging to the same category as metasilicic acid and metasilicates (augite, hornblende), titanic acid, metastannic acid, pyrophosphoric acid, metantimonates, normal and acid sulphates, chromates, &c., whilst the acid $H_2I_2O_8$ corresponds to the metaphosphates, common antimonates, pyrosulphates, dichromates, perchlorates, and permanganates.

To explain the constitution of these compounds by the quantivalence of the elements, we have to assume that silicon and titanium are *tetrads*, phosphorus and vanadium—*pentads*, sulphur and chromium—*hexads* and chlorine and manganese *heptads*. The composition of these hydrates can be expressed by the general formula:

$$H_{2n}X_2O_{v+n}, \text{ or } H_nXO_{\frac{v+n}{2}}.$$

X being the atomic weight of an element, v its quantivalence as deduced from the highest oxide, and n a whole number, which generally does not exceed 4. The following table shows that this formula not only expresses the composition of the above compounds, but also that of the oxides, hydrates, or salts of other elements:—

	$v = 1$	$v = 2.$	$v = 3.$	$v = 4.$	$v = 5.$	$v = 6.$	$v = 7.$
$n = 0$	Na_2O Cu_2O	Mg_2O_2 Zn_2O_2	Al_2O_3 B_2O_3	Si_2O_4 Ti_2O_4	P_2O_5 V_2O_5	S_2O_6 Cr_2O_6	(Cl_2O_7) (Mn_2O_7)
$n = 1$	$H_2Na_2O_2$ $H_2K_2O_2$ $H_2Pb_2O_2$ $H_2Cr_2O_2$		$H_2Al_2O_4$ (Diaspore) $MgAl_2O_4$ (Spinell) $H_2B_2O_4$	$H_2Si_2O_5$ (Opal ?)	$H_2P_2O_6$ SrV_2O_6 $FeNb_2O_6$ $K_2Sb_2O_6$ $FeTa_2O_6$	$H_2S_2O_7$ $K_2Cr_2O_7$ $Na_2Mo_2O_7$	$H_2Cl_2O_8$ $H_2Mn_2O_8$
$n = 2$		$H_4Mg_2O_4$ $H_4Ca_2O_4$ $H_4Zn_2O_4$ $H_4Sr_2O_4$ $H_4Cd_2O_4$ $H_4Ba_2O_4$	$H_2Ag_2B_2O_5$	$Ca_2Si_2O_6$ (Wollastonite) $Fe_2Ti_2O_6$ (Titaniferous iron) $H_4Sn_2O_6$ (Metastannic acid)	$H_4P_2O_7$ $Ag_4V_2O_7$ $H_4Nb_2O_7$ $K_4Sb_2O_7$	$H_8KS_2O_8$ $K_4Cr_2O_8$ $K_4Se_2O_8$ $Pb_2Mo_2O_8$ $K_4Te_2O_8$ $Ca_2W_2O_8$	$K_4I_2O_9$
$n = 3$			$H_6Al_2O_6$ (Hydrargillite) $H_6B_2O_6$ (Sassolin)	$H_4CaSi_2O_7$ (Okenite)	$H_6P_2O_8$ $Ag_6V_2O_8$ $Ag_6As_2O_8$		$Pb_3I_2O_{10}$
$n = 4$				$Zn_4Si_2O_8$ (Willemite) $Be_4Si_2O_8$ (Phenakite)	$H_8Sb_2O_9$ (Antimony ochre from Constantine)	$H_8S_2O_{10}$ $H_4Li_4S_2O_{10}$ $H_8W_2O_{10}$	$Zn_4I_2O_{11}$
$n = 5$						$H_8K_2Te_2O_{11}$	$Ag_{10}I_2O_{12}$ $H_{10}I_2O_{12}$

The composition of the hydrates corresponding to the lower oxides may be expressed by analogous formulæ:—

$$H_{2n}X_2O_{v+n-2}, \text{ or } H_nXO_{\frac{v+n}{2}-1}$$

$$H_{2n}X_2O_{v+n-4}, \text{ or } H_nXO_{\frac{v+n}{2}-2}, \text{ \&c,}$$

The first of these includes the nitrites, phosphites, sulphites, and chlorates, and the second gives the composition of Schützenberger's hyposulphurous acid, chlorites, &c.

Similar formulæ may also be used for expressing the composition of the chlorides and oxychlorides. But whether in these compounds v has the same value as in the oxides and hydrates cannot be decided at present. The fact that in most cases we do not know the chlorides corresponding to the highest oxides is no reason why the value of v should not be the same for each element.

It appears, however, more convenient for the present not to identify this number with the quantivalence, and to call this empirical value "the index of affinity," in order to prevent the influence of any preconceived opinion.

The above classification of inorganic compounds leads to a system of homologous and heterologous series, being quite analogous to that which Gerhardt has introduced with so much success into organic chemistry.

It is, however, not yet possible to carry out such a system completely; new critical researches are required, and chiefly of those compounds which neither fit into the dualistic-electro-chemical nor into the typical system. It is therefore most desirable that chemists should again pay more attention to the study of inorganic chemistry, which lately has been so much neglected. The author and his pupils are at present engaged in a new examination of the chlorides and oxychlorides of sulphur and molybdenum.

C. S.

Contributions to the Theory that Oxygen becomes Active during Slow Oxidation. By H. Fudakowski (Deut. Chem. Ges. Ber., vi, 106—109).

When a small quantity of petroleum (boiling at 30° to 100° and upwards, and of sp. gr. 0·67 to 0·68 at 22°) is placed in a capacious flask which is frequently opened and shaken, it acquires oxidising properties, and the air contained in the flask gives the ozone reaction. This occurs in a few days at the summer temperature if the vessel is exposed to the direct rays of the sun, and more slowly at a lower temperature and in diffused daylight. The slow evaporation appears to play an important part. This petroleum, shaken up with a solution of potassium iodide liberates iodine from it, and paper prepared with potassium iodide and starch-paste acquires a blue colour when exposed to the air in the flask. It also decolorises indigo, gives a blue colour to guaicum extract, and exhibits the other reactions of active oxygen. When the petroleum is shaken up with water, the latter remains

neutral, and when tested shows the presence of hydrogen peroxide; but if the petroleum has remained for a long time in contact with the air, it acquires an acid reaction which it communicates to water when agitated with it. The aqueous solution is found still to contain hydrogen peroxide, but it also reduces silver nitrate, thus indicating the presence of formic acid. Petroleum readily absorbs ozone—liberated from potassium permanganate by the action of sulphuric acid—and when agitated with water gives to it an acid reaction, whilst the solution reduces silver salts, but the petroleum is not at once capable of liberating iodine from potassium iodide solution. When allowed to stand for 24 hours however, it acquires that property, and if it be now agitated with water, the solution gives the characteristic reactions of hydrogen peroxide.

Similarly, pure benzene prepared from benzoic acid, and that portion of light coal oil boiling between 80° and 100°, exhibit the same power of rendering oxygen active. Pure phenol mixed with water also acquires, in contact with air, the power of turning paper blue which has been prepared with potassium iodide and starch paste.

C. E. G.

Amount of Carbonic Acid in Atmospheric Air.

By W. Henneberg (Landw. Versuchs-Stationen, xvi, 70).

The amount shown by F. Schulze's determinations (*Chem. Soc. Jour.* [2], x, 668) was lower than that usually supposed; the author's experiments made during the summer of 1872 at Weend confirm Schulze's results. Seventeen determinations on a large scale, made for the purpose of respiration experiments, gave a mean of 3·2 volumes of carbonic acid per 10,000 of air, at 0°, and a pressure of 760 mm.

R. W.

Basicity and Constitution of Periodic Acid.

By Julius Thomsen (Deut. Chem. Ges. Ber., vi, 2—9).

By treating a dilute solution of periodic acid with different proportions of potassium hydrate, it is found to evolve most heat when the ratio is $IO_6H_5 : 2KHO$. The number of heat-units per molecule of alkali is then 13300 which, like those expressing the heat of neutralisation of many acids, lies between the limits 13150 and 13750. A further, but proportionately much smaller evolution of heat takes place on the addition of more alkali, but the same phenomenon occurs with phosphoric, arsenic, sulphurous, carbonic, and other acids, when more than the normal quantity of alkali is added. Periodic acid is therefore proved by dynamic analysis to be bibasic, supposing its molecule to be IO_6H_5.

Since, however, the three hydrogens in the formula $IO_4H_2(OH)_3$, not normally basic, are in many salts easily expelled by heat in the form of water, this formula must be doubled, and written $H_4I_2O_9.3H_2O$, as Rammelsberg has been led to write it. The acid is therefore quadribasic and decatomic, and its heat of neutralisation is 4×13300 units.

The normal periodates have the formula—

$$R'_4I_2O_9.3H_2O, \text{ or } R''_2I_2O_9\,3H_2O,$$

in which the water may be partly or entirely expelled by heat. They are the semi-periodates of Rammelsberg. The solution of the normal potassium salt has an alkaline reaction; a solution of neutral reaction is obtained by adding three molecules of potassium hydrate to the quadribasic molecule of the acid, but the solution is unstable, and deposits a crystalline salt even when dilute.

There are three series of basic periodates which the author styles monobasic, bibasic, and tribasic, according as the hydrogen of one, two, or three of the molecules of water, in addition to the normally basic hydrogen, are replaced by metals:—

Monobasic	$Pb_3I_2O_{10}.2H_2O$.
Bibasic	$Zn_4I_2O_{11}.H_2O$.
Tribasic	$\left\{\begin{array}{l} Ba_5I_2O_{12} \\ Ag_{10}I_2O_{12}. \end{array}\right.$

Periodic acid also forms a series of acid salts, the general formula of which is $R'_2I_2O_8$, and which, with the exception of the magnesium and strontium salts, are anhydrous. The constitution of these salts must be regarded as distinct from that of the normal and basic salts. For those which are anhydrous are isomorphous with the perchlorates, and the formula of these must be $R'_2Cl_2O_8$, since potassium perchlorate is isomorphous with the permanganate $K_2Mn_2O_8$. Besides this, the formation of the acid salts is attended with a remarkable thermic phenomenon, which this view of their constitution explains. The conversion of the normal potassium salt into the acid salt is attended with the absorption of 8150 units of heat per molecule of alkali, an amount far in excess of that occurring with any other acid—the corresponding formation of the acid salt of sulphuric acid causing the absorption of only 935 units, of selenic acid of only 432, and of hydrofluoric and oxalic acids of only 290. Now this unusual disappearance of heat may fairly be attributed to its consumption in the splitting up of the tetrabasic molecule of the acid in presence of only two molecules of potassium hydrate, in such a way that the three water-molecules and another one derived from the two remaining hydroxyls, separate:

$$H_4I_2O_9.3H_2O = H_2I_2O_8 + 4H_2O.$$

E. D.

Constitution of Periodic Acid. By A. Basarow (Deut. Chem. Ges. Ber., vi, 92—94).

Thomsen, in his recently published memoir on periodic acid, has cleared the way to a correct conception of the constitution of this acid in defining it to be quadribasic and decatomic. But the author cannot agree with him in doubling the formula H_5IO_6, nor in his views as to the constitution of the acid and its salts.

Periodic acid appears to be bibasic and pentatomic $(HO)_2IO(OH)_3$.

Three of the hydrogens are like the alcoholic hydrogen of those organic acids the atomicity of which exceeds their basicity, and, like that hydrogen, can undergo metallic substitution. The salts of $(HO)IO_3$ the author considers to be, not acid salts of periodic acid, but normal salts of meta-periodic acid, bearing the same relation to the periodates that the metaphosphates do to the phosphates. The silver salt $(AgO)_2IO(OH)_3$ becomes at 200° a salt of the acid $\left.\begin{matrix}(HO)_2IO_2\\(HO)_2IO_2\end{matrix}\right\}O$, and this may be regarded as pyro-periodic acid. In all these compounds the iodine is septivalent.

E. D.

Boiling-point of Liquefied Sulphur Dioxide. By I. PIERRE (Compt. rend., lxxvi, 214).

MELSENS has recently stated that he was unable to determine accurately the boiling-point of liquefied sulphur dioxide; the author recalls the results of his determinations made twenty-six years ago, which indicated −8° as the boiling-point. The apparatus employed was very simple, consisting of a thin glass test-tube, 2·5 to 3 centimeters in diameter, fitted with a cork perforated with two holes, one to allow of the passage of the stem of the thermometer, the other to contain a tube to carry off the gaseous sulphur dioxide. The temperature of the air being above that of the (previously cooled) liquefied dioxide, the liquid speedily begins to boil, but the rapid ebullition soon slackens from the cooling effect produced by the vaporisation; thus a series of alternate bursts of ebullition and slackening ensue, during which the thermometer varies only by 0·15° to 0·20°, the fluctuations being smaller if the deposition of dew outside the tube be prevented by covering it with flannel. The experiment is made so easily, that it forms a convenient lecture illustration. The same mode of determination is applicable to all such liquefied gases as can be kept in an open vessel, *i.e.*, which do not receive more heat from the surrounding media in a given time than is required to furnish the heat rendered latent by the volatilisation of that part of the liquid which evaporates during that period.

C. R. A. W.

Production of Sulphuryl Chloride from Sulphuric Anhydride and Boron Chloride. By G. GUSTAVSON (Deut. Chem. Ges. Ber., vi, 9—11).

SULPHURYL chloride, SO_2Cl_2, has been obtained by the action of sunlight upon a mixture of sulphurous anhydride and chlorine, but not from sulphuric anhydride by the action of either carbon tetrachloride, phosphorus chlorides, or sulphur chlorides. Michaelis has consequently been led to doubt the possibility of forming it from sulphuric anhydride. It can, however, be obtained by acting on this body with boron chloride. One atom of boron chloride and two of the anhydride heated together at 120° for about eight hours, are converted into boron sulphate and sulphuryl chloride, which can be separated by distilling off the latter:

$$2BCl_3 + 4SO_3 = 3SO_2Cl_2 + B_2O_3.SO_3.$$

The boron sulphate was not analysed; it is a solid body, reacting violently with water generating sulphuric and boracic acids. Heated, it fuses with spurting, sulphuric anhydride escaping in vapour, and boric anhydric remaining behind.

Boron bromide yields by the same treatment, not sulphuryl bromide, but bromine and sulphur dioxide. Silicium chloride yields $S_2O_5Cl_2$.

E. D.

On the Union of Ammonia Nitrate with Ammonia.

By EDWARD DIVERS (Proc. Roy. Soc., xxi, 109—111).

AMMONIA nitrate deliquesces in ammonia gas at ordinary temperatures and pressures, forming a solution of the salt in liquefied ammonia.

The liquid obtained varies in composition according to the temperature and pressure. At a temperature of 23° and the pressure of the atmosphere, it consists of about four parts of nitrate to one of ammonia by weight; but under greater pressure, or at lower temperatures, much more ammonia can be condensed by the nitrate. At 0° and the pressure of the atmosphere, two parts of nitrate can condense one part of ammonia. Like an aqueous solution, the liquid boils when heated, and, when nearly saturated with the nitrate, deposits crystals of it when cooled. It can also, like an aqueous solution, be heated above its boiling-point without boiling, and become supersaturated with the salt without crystallising. During its decomposition, cold is manifested, and during its formation heat is evolved, but not to a great extent, because the heat given out by the liquefaction of the ammonia is nearly all used up in the liquefaction of the nitrate.

The specific gravity of the liquid varies, of couse, with its composition. When it consists of two of nitrate to one of ammonia, it has a specific gravity of 1·0725; when it consists of four of nitrate to one of ammonia, it has a specific gravity of nearly 1·200. Its specific gravity can be calculated from its composition, by taking for the purpose 1·5245 as the specific gravity of the nitrate, and ·671 as that of the ammonia.

In its rate of expansion by heat, the liquid resembles others which exist as such at ordinary temperatures, rather than those which, like ammonia itself, are retained as such only by great pressure. Its expansivity increases with the quantity of ammonia present.

Its action upon a great number of substances, principally inorganic, has been tried, and found to be for the most part like the actions of dry ammonia and ammonia nitrate conjoined. The nitrate appears to undergo double decomposition with most salts, and the ammonia to unite with nearly all, including the salts of magnesium, aluminium, iron, and manganese. The ammoniated compounds which do not dissolve in the liquid are very bulky. Nitrates, chlorides, iodides, and bromides are either soluble or are decomposed into soluble chlorides, &c., of ammonium, and insoluble ammoniated compounds of the metals. Sulphates, oxalates, chromates, and arsenites are insoluble, and phosphates are nearly so. Phosphoric and chromic anhydrides do not act upon the liquid with the energy that might be expected, but combine

with the ammonia. Iodine dissolves freely. Bromine generates nitrogen. Lead salts, including sulphate, chloride, iodide, and oxide, are freely soluble as ammoniated compounds. Platinous chloride dissolves freely as tetrammonio-platinous chloride. Potassium salts are very sparingly soluble. Alkalis and their carbonates decompose the nitrate; so do litharge, lime, and baryta. Calomel is converted into metallic mercury and a soluble ammoniated mercuric compound. Potassium, sodium, zinc, and cadmium dissolve without liberating gas, by reducing the nitrate to nitrite, potassium inflaming. Magnesium slowly dissolves, liberating a little hydrogen, reducing the nitrate, and becoming partly converted into Beetz's black suboxide of magnesium. Methyl iodide is decomposed; butyric ether and chloroform are sparingly soluble without decomposition. Ether is insoluble, but by its contact causes the liquid to break up into its two constituents.

It is a good electrolyte, ammonia and hydrogen appearing at the negative electrode, and nitrogen and ammonia nitrate at the positive electrode.

Positive electrodes of silver, lead, copper, zinc, and magnesium are dissolved by the liquid as (ammoniated) nitrates. A positive electrode of mercury is converted into a compound almost insoluble in the liquid. When the electrode is acted upon, the generation of nitrogen does not take place.

E. D.

Allotropic Transformations of Phosphorus.

By TROOST and HAUTEFEUILLE (Compt. rend., lxxvi, 76 and 219).

THE authors have previously established that the transformation of cyanic acid into cyamelide obeys different laws according as the compound is in the state of gas or of liquid, taking place much more rapidly and completely in the latter case. When the tension of the vapour becomes diminished to a certain minimum value, varying for each actual temperature, the transformation ceases; this tension is spoken of as *the tension of transformation*, and is established only after the lapse of some time.

Precisely the same laws hold good in the case of phosphorus; the liquid element, at 280° for instance, is perfectly comparable with liquid cyanic acid, becoming wholly transformed into red phosphorus; the vapour given off at 260° is stable; but that formed at higher temperatures becomes slowly and partially converted into red phosphorus, the production of which ceases when the tension attains a given minimum: the rapidity with which this change is produced is greater the higher the temperature.

At 360° the mean of several experiments gives 1·4 gram as the weight of a litre of phosphorus vapour which remains in the vaporous state after two hundred and forty hours' heating; at 440° the weight is 3·7 grams after thirty hours' heating; whence it is calculated that the tension of transformation is 0·6 atmospheres at 360°, and 1·75 atmospheres at 440°. This latter value was obtained by Lemoine in 1871, this chemist finding the same result whether yellow or red phosphorus was employed as point of departure, just as the author found in 1868

that the tension of transformation of cyanic acid is the same whether cyanic acid itself or cyamelide be employed as starting point.

The maximum tensions of phosphorus vapour at these temperatures are much higher than the tensions of transformation: to prevent phosphorus boiling at 360°, a pressure of 3·2 atmospheres must be exerted; at 440° a pressure of 7·5 atmospheres.

Other experiments made in tubes heated from the top downwards in a current of mercury or sulphur vapour, the phosphorus contained in the tubes being weighed after several hours' heating, yielded the following values for the maximum tensions of phosphorus vapour: at 360°, 3·2 atmospheres; at 440°, 7·3 atmospheres; values nearly identical with those obtained by the first method.

To determine the maximum elastic force of phosphorus vapour, the authors employed the method above mentioned, viz., heating a tube terminating in a bulb and containing phosphorus in a *descending* current of mercury or sulphur vapour, the bulb and tube being sealed and exhausted of air before commencing the experiment; for higher temperatures the tubes were gradually raised into a vertical cylinder of iron closed at top and heated to a uniform temperature by a bath of melted lead. The following results were obtained—

The maximum tension of phosphorus vapour is independent of the excess of phosphorus used, as long as the temperature does not exceed 520°, but above this temperature the maximum tension is not obtainable, because the transformation of the liquid phosphorus takes place so rapidly that there is not time for the maximum tension to become established; whilst at temperatures above 550°, the tension observed is no greater than the tension of transformation, because the transformation of the liquid phosphorus takes place more rapidly than its evaporation: at 580° this pressure amounts to 56 atmospheres, the greatest pressure which the glass used could bear.

Temperature.	Maximum tension.	Tension of transformation.
360°	3·2 atmospheres.	0·6 atmospheres.
440°	7·5 "	1·75 "
487°	——	6·8 "
494°	18·0 "	
503°	21·9 "	
510°	——	10·08 "
511°	26·2 "	
531°	——	16·0 "
550°	——	31·0 "
577°	——	56·0 "

It should hence result that when phosphorus is volatilised in a vessel not at a uniform temperature throughout, the deposit of red phosphorus formed by the transformation of the vapour should be produced at the hottest part only; by employing a long horizontal tube containing red phosphorus in the middle, sealed at each end after exhausting the air, and heated to different temperatures in different parts, the hottest part being the middle, the authors succeeded in so regulating these temperatures with respect to one another, that whilst only colourless liquid phosphorus was formed at one end, the other end was covered internally

with an orange-red translucent film of amorphous phosphorus; to obtain this result the temperatures were—

Middle of tube about	500°
End where orange phosphorus appeared (heated in mercury vapour)	350°
End where only liquid ordinary phosphorus appeared (heated in vapour of mercury bromide)	324°

In another experiment similar results were obtained when the ends were at the temperatures 440° (sulphur boiling at 760 millimeters pressure) and 420° (sulphur boiling at 470 millimeters pressure) respectively. Hence the transformation of phosphorus vapour is in all respects analogous to that of the vapour of cyanic acid.

The transformation of liquid phosphorus and that of its vapour, therefore, obey entirely different laws; and there is a great distinction between the phenomena of *isomeric transformation* of a vapour and *condensation* of that vapour: the vaporisation of a body considered solely under two physical aspects (as water and ice) for example, is limited by one single vapour-tension, whilst the volatilization of a substance that undergoes isomeric (or allotropic) modification, as well as change of state, is subject to two different tensions.

C. R. A. W.

Spontaneously Inflammable Hydrogen Phosphide from Phosphonium Iodide. By C. Rammelsberg (Deut. Chem. Ges. Ber., vi, 88).

Hydrogen phosphide liberated from phosphonium iodide by solution of potassium hydrate is considered not to be spontaneously inflammable (*Chem. Soc., J.* [2], ix, 305). The author has, however, observed that it sometimes takes fire spontaneously.

E. D.

The Atomic Weight of the Cerium Metals, and the Salts of Ceroso-ceric Oxide. By C. Rammelsberg (Deut. Chem. Ges. Ber., vi, 84—88).

In consequence of the variation of some of the results of the investigation of certain cerium salts by Zschiesche (*J. prakt. Chem.*, cvii, 65) and by Holzmann (*ibid.*, lxxv, 330) from those of his own researches (*Pogg. Ann.*, cviii, 40), and also on account of the views put forward by Mendelejeff as to the atomic weights of cerium, didymium, and lanthanum, the author has re-examined some of the salts of cerium. His recent investigation confirms the accuracy of his former results, and these results, together with other points in the history of the cerium metals, throw great doubt on the correctness of Mendelejeff's views.

The examination of the brown red ceroso-ceric sulphate has given results agreeing with the former ones obtained, suggesting the formula $Ce_5S_6O_{24}$ + 18aq., excepting in the quantity of water, which is better represented by a formula containing 3 aq. additional, namely:

$$Ce_5S_6O_{24} + 21aq. = \left.\begin{matrix} 3CeSO_4 \\ Ce_2S_3O_{12} \end{matrix}\right\} + 21aq.$$

Zschiesche expresses its composition by the formula—

$$Ce_7S_9O_{36} + 27aq. = \left.\begin{matrix} 3CeSO_4 \\ 2Ce_2S_3O_{12} \end{matrix}\right\} + 27aq.$$

The two formulæ require almost the same amount of cerous sulphate and of ceroso-ceric oxide; and, although there is some difference in the amounts of SO_3 required, this is of little use in determining the correct formula, because an exact estimation of the sulphuric acid cannot be made, as the salt only separates from solution in strong sulphuric acid. The choice of the formula must therefore rest upon the quantity of oxygen which the salt gives up in passing to the state of cerous sulphate. In Zschiesche's formula this is represented by the centesimal 1·6; in the author's by 1·18. Therefore, as the author still gets from 0·8—1·12 per cent., and Zschiesche also gets from 0·8—1·06 per cent., the author still maintains the correctness of his own formula.

The double sulphate of ceroso-ceric oxide and ammonia, occurring in red, well-marked monoclinic crystals, is beyond dispute a homogeneous salt and not a mixture, its formula being,

$$\left.\begin{matrix} 9(NH_4)_2SO_4 \\ CeSO_4 \\ 2Ce_2S_3O_{12} \end{matrix}\right\} + 12aq.$$

The double nitrates of cerium with magnesium and with zinc, which crystallise in isomorphous rhombohedral forms from a mixture of the solution of ceroso-ceric hydrate in nitric acid with magnesium nitrate and zinc nitrate respectively, have a fine red colour; but this is derived from the red ceric mother-liquor. On recrystallisation, they are obtained nearly colourless. Holzmann's formula for them—

$$\left.\begin{matrix} 2R''N_2O_6 \\ CeN_2O_6 \\ Ce_2N_6O_{18} \end{matrix}\right\} + 15aq.$$

is incorrect. They are cerous compounds—

$$\left.\begin{matrix} R''N_2O_6 \\ CeN_2O_6 \end{matrix}\right\} + 8aq.$$

like the corresponding isomorphous salts of nickel, cobalt and manganese.

Mendelejeff has proposed to raise the atomic weight of cerium from 92 to $\frac{3}{2}$. 92, or 138, and, like H. Rose, to consider the higher oxide as a single oxide, CeO and Ce_3O_4 then becoming Ce_2O_3 and CeO_2. He also makes a similar alteration in the atomic weight of didymium, and writes its oxide Di_2O_3 instead of DiO; while, lastly, he changes the atomic weight of lanthanum and writes its oxide LaO_2 instead of LaO. Thus didymium oxide is made analogous to cerous oxide, and lanthanum oxide to the higher cerium oxide.

That Ce_3O_4 is $CeO.Ce_2O_3$, and not a simple oxide (CeO_2; Mendelejeff) is shown by the composition of the brown-red sulphate and of the ammonio-sulphate, which are compounds of Ce_5O_6 and Ce_5O_7 respectively, and not of Ce_3O_4 (CeO_2; Mend.). It is true that $Ce_5O_6 =$

$Ce_6O_9(Ce = 138)$ may be written thus: $Ce_2O_3 + 3CeO_2$, but even this cannot be done with $Ce_6O_7 = Ce_{10}O_{11}(Ce = 138)$.

Mendelejeff compares the reduction of the higher oxide to cerous oxide with that of TiO_2 to Ti_2O_3; but against this analogy is the fact that the higher oxide of cerum liberates chlorine from hydrochloric acid. Then, too, cerous oxide decomposes a solution of ammonium chloride, while a sesquioxide R_2O_3 does not do so. Ceroso-ceric oxide crystallises like R_3O_4 in the regular system: as CeO_2 it ought to take the form of TiO_2 and ZrO_2.

With regard to didymium and lanthanum, their isomorphism with cerium is beyond question, so that their oxides must be analogous. The chlorides have the formulæ Ce_2Cl_6, Di_2Cl_6, and $LaCl_4$ when $Ce = 138$; yet they resemble each other in the highest degree, are with 4aq. apparently isomorphous, and are quite distinct from the chlorides R_2Cl_6 and RCl_4, which are volatile and decomposed by water.

E. D.

Decomposition (Dissociation) of Mercuric Oxide by Heat.

By JACOB MYERS (Deut. Chem. Ges. Ber., vi, 11—16).

THE author has heated the carefully-prepared red modification of mercuric oxide for long periods in tubes connected with a Geissler's pump, and finds, as he expected, from the looseness of the combination between mercury and oxygen, that it accords but partially with Pfaundler's theory of dissociation.

Evidence of decomposition was obtained at 150°, but at 240° the tension of the oxygen amounted to only 2 mm., and at 293° only to $2\frac{1}{2}$ mm. At these temperatures the maximum tension is soon reached, so that the behaviour of the oxide is here conformable with Pfaundler's theory. But at 350° and temperatures above this, the tension was found to increase continually, though very slowly, and never reach a maximum, although the experiments lasted for many hours, and the effects of longer heating were imitated by admitting oxygen into the apparatus. The rate of the development of oxygen diminished, however, as the experiment proceeded, owing, no doubt, to the effect of the increasing tension of the gas. The behaviour of the oxide is also exceptional, in that the tension is not diminished by cooling, whether rapidly or slowly.

E. D.

Spontaneous Disintegration of Lead and Bismuth Alloys.

By VOGEL (Ber. der K. b. Akad. d. Wissenschaften, 1872, 218—222).

SOME casts of coins in the University cabinet were found to be greatly oxidised, and the metal in parts so rotten as to crumble between the fingers. The alloys were lead and bismuth, containing 34, 14, and 12 per cent. of the latter metal. The oxidised portion contained much lead carbonate, and some bismuth oxide. The action of the atmosphere and the tendency of bismuth to assume a crystalline form, are supposed to have occasioned the disintegration.

The author prefers to separate lead and bismuth by adding excess of sulphuric acid to the nitric acid solution; he then evaporates to perfect dryness, treats the residue with sulphuric acid, after some hours adds water, and separates the lead and bismuth sulphates by filtration. The volatilising points of the bismuth and lead chlorides are too near to allow of their exact separation by heating in a current of chlorine.

R. W.

The Purple of Cassius. By H. Debray (Compt. rend., lxxv, 1025—1027).

Macquer having observed that the purple of Cassius was deeper in colour the more gold it contained, considered it to be a mixture of stannic hydrate and metallic gold. But Proust, finding that, when moist, it dissolved in ammonia, and that it did not yield gold when treated with mercury, looked upon it as a true combination, consisting of aurostannous stannate, mixed with varying proportions of stannic hydrate.

The author considers both views to be wrong, and regards the purple as a "lake" of stannic acid, coloured by metallic gold; and that, just as ordinary lakes will not yield up their colours to water, so the gold is prevented by its union with the acid from being dissolved out by mercury. Instead of preparing the purple in the usual way, it may be obtained by first precipitating stannic oxide by boiling together stannic chloride and sodium acetate, then adding gold chloride and potassium oxalate, and again boiling, when metallic gold will be precipitated upon the oxide. A similar colour is produced if alumina be substituted for stannic oxide. Thus it is considered as proved that the purple is simply an oxide coloured by gold. That the purple should be soluble in ammonia is not surprising, if it be admitted to be chiefly made up of stannic oxide, which is soluble in ammonia in the cold. Elevation of temperature and desiccation, are preventives to the solubility both of stannic oxide and of the purple. Moreover, the solution, which always appears turbid by reflected light, slowly deposits metallic gold. The latter could not, therefore, have been present as an oxide, since ammonia, in acting upon oxides of the precious metals, gives rise to products more or less complex, but the metal is never set free.

In the assay of silver containing a little gold and tin, there is often observed, on dissolving the metal in nitric acid, a substance very similar in appearance to the purple of Cassius. It is not, however, soluble in ammonia, and the author thought that this might be due to the metal having been dissolved in hot acid, just as stannic oxide, obtained by oxidising tin with hot acid, is also insoluble in ammonia. He therefore attacked, with nitric acid, at a very gentle heat, an alloy of silver, gold, and tin, and obtained a purple residue quite soluble in ammonia, showing the identity of this residue with the ordinary purple.

It should be added that the author seems to consider a "lake" as standing midway between a mixture and a combination.

B. J. G.

Note on Meta-vanadic Acid. By B. W. Gerland (Chem. News, xxvii, 92).

A solution of copper vanadate in aqueous sulphurous acid, after part of the latter is removed by boiling, deposits brilliant yellow crystals, quite uniform in appearance, and containing cupric oxide, vanadic acid, and sulphurous acid. These crystals rapidly change under the influence of air, and become dark green in colour. Although formed in a solution of sulphurous acid, they nevertheless decompose when treated, after separation from their mother liquor, with fresh sulphurous acid, so that two kinds of crystals, brown and orange-yellow, are produced. An excess of sulphurous acid dissolves the former and leaves the latter intact. After being washed and dried, they form microscopic scales of beautiful lustre and of a deep yellow-orange colour: they are free from copper and sulphur, and perfectly unalterable in the air. Heated to 130°, they lose no weight, but at a low red heat water is given off, and the residue consists of vanadium pentoxide, which fuses and crystallises after cooling. The composition of the substance, after being dried over vitriol is—

Water (loss by heating)	8·73
Vanadium pentoxide............	91·06
Impurities	0·21
	100·00

These numbers correspond with the formula of meta-vanadic acid, VHO_3.

This vanadium bronze is essentially distinguished from the amorphous, brick-red hydrated vanadic acid by its indifference to reagents.

J. B.

Mineralogical Chemistry.

The Red Zinc Oxide of New Jersey. By A. A. Hayes (Amer. Jour. Science [3], iv, 191—198).

The rich red colour of this mineral was thought by Berthier, in 1834, to be due to manganese dioxide. In 1845 the author concluded that the colouring matter was specular iron ore. Dana accepted this opinion till the 5th edition of his *Mineralogy* was issued, in which he stated that, even with a high power, he could find no scales of red iron oxide. Careful examination now shows that the colour is produced partly by specular iron scales and partly by a micaceous mineral containing silicon, zinc, calcium, iron, and molybdenum. This amounts to about 1 per cent., the remaining 99 per cent. being zinc oxide and manganous oxide.

B. J. G.

On some New Minerals containing Uranium.

By CLEMENS WINKLER (J. pr. Chem. [2], vii, 1—14).

THE minerals described in this paper were found at the opening of the "White Hart" mine, near Schneeberg, in 1871. The methods of analysis adopted by the author are given at length.

Uranosphærite. The brick-red hemispherical masses of this body decrepitate when heated, and break up into silky needles, having a transient brown colour. Two analyses of it gave the following numbers:—

U_2O_3.	Bi_2O_3.	H_2O.
50·32	44·12	5·56 = 100·00
50·88	44·34	4·75 = 99·97

corresponding with the formula—

$$Bi_2O_3.2U_2O_3 + 3H_2O, \text{ or } \left.\begin{matrix}(UO)_4\\Bi_2\end{matrix}\right\}O_6 + 3H_2O.$$

Walpurgin. Crystals of this body when heated to redness, assumes a brown colour, changing to dark-yellow on cooling, but they neither decrepitate nor change their form, nor yet lose brilliancy. When treated with nitric acid, they leave a white residue of bismuth arsenate, which dissolves on addition of hydrochloric acid. Two analyses gave—

Bi_2O_3.	U_2O_3.	As_2O_5.	H_2O.
61·43	20·29	11·88	4·32 = 97·92
59·34	20·54	13·03	4·65 = 97·56

Hence the formula is—

$$5Bi_2O_3.As_2O_5 + 3U_2O_3.As_2O_5 + 10H_2O, \text{ or } \left.\begin{matrix}(AsO)_2\\Bi_5(UO)_3\end{matrix}\right\}O_{12} + 5H_2O.$$

Trögerite. The yellow crystals of this mineral give off water when heated, and acquire at the same time a transient golden-brown colour and brilliant lustre, but do not change their form. The ignited trögerite when moistened with water breaks up into small glittering laminæ, with slight detonation and rise of temperature. Three analyses furnished the following numbers:—

U_2O_3.	As_2O_5.	H_2O.
63·44	18·48	18·08 = 100 00
62·42	18·83	18·75 = 100·00
63·76	19·64	14·81 = 98·21

which correspond approximately with the formula—

$$3U_2O_3.As_2O_5 + 12H_2O, \text{ or } \left.\begin{matrix}(AsO)\\(UO)_3\end{matrix}\right\}O_3 + 6H_2O.$$

Zeunerite. A mineral corresponding to copper-uranite, with arsenic acid in place of phosphoric acid. It gave on analysis—

CuO.	U_2O_3.	As_2O_5.	H_2O.
7·49	55·86	20·94	15·68 = 99·97

which numbers correspond with the formula—

$$CuO.2U_2O_3.As_2O_5 + 8H_2O, \text{ or } \left.\begin{matrix}(AsO)_2\\ Cu(UO)_4\end{matrix}\right\} O_6 + 8H_2O.$$

The author, for the sake of comparison, analysed also a specimen of copper-uranite from Redruth, and found it to contain arsenic acid partially replacing the phosphoric acid of the normally constituted mineral. Another specimen of copper-uranite found very near to the "White Hart" mine was, however, quite free from arsenic.

Uranospinite. Together with zeunerite there occurred small quantities of another mineral of light-green colour, which was found on analysis to correspond with calcium-uranite having arsenic acid in place of phosphoric acid. The numbers found were—

CaO.	U_2O_3.	As_2O_5.	H_2O.
5·47	59·18	19·37	16·19 = 100·21

Hence the formula—

$$CaO.2U_2O_3.As_2O_5 + 8H_2O, \text{ or } \left.\begin{matrix}(AsO)_2\\ Ca(UO)_4\end{matrix}\right\} O_6 + 8H_2O.$$

The author has found that the last two minerals (zeunerite and uranospinite) may be formed artificially by mixing a solution of precipitated copper carbonate, or of lime, in excess of arsenic acid with a solution of uranium nitrate. The mixed solutions gradually deposit rectangular crystalline laminæ having the composition of the natural minerals.

J. R.

Composition of the Olivine and Serpentine of Snarum.

By A. HELLAND (Pogg. Ann., cxlviii, 329—335).

THE serpentine of Snarum contains a considerable number of grains of fresh unweathered olivine embedded in its mass. Those grains are sharply separated from the serpentine, no gradual transition from olivine to serpentine being apparent, and when the serpentine is coarsely pulverised, the grains of olivine may be picked out quite free from serpentine.

Analysis of the olivine and serpentine gave the following results:—

	Olivine.	Oxygen.	Serpentine.	Oxygen.
SiO_2	41·32	22·04	42·72	22·78
M_2O_3.......... .	0·28	0·13	0 06	0·03
FeO	2·39	0·53	2·25	0·50
CrO	0·05	0·01	trace	—
MgO............	54·69	21·87	42·52	17·01
Loss by ignition ..	0·20		13·39	11·90
	98·93		100·94	
Specific gravity ..		3·22		2·53

The oxygen-ratios are: in olivine, 1·01 : 1 or 1 : 1; in serpentine,

3·07 : 4 : 2·09 or 3 : 4 : 2. The olivine is very pure; it is unusually free from iron, and has a very low specific gravity.

If olivine can be converted into serpentine without alteration of volume, the proportions in which the constituents are separated and taken up by the pseudomorphic process, can be determined. The assumption that this transformation has taken place without change of volume is perhaps not absolutely true, and the results of the calculation are therefore only approximate; nevertheless, they probably give to a certain extent a true picture of the transformation. If we multiply the specific gravity into the percentage of the constituents, we obtain (reducing the constituents to 100 parts)—

	In a cubic centimeter. Olivine.	Serpentine.	Separated ÷. Taken up +.	In percentages of Olivine.
SiO_2....	1·345 gr.	1·071 gr.	÷ 0·274 gr.	÷ 8·51
M_2O_3 ...	0·009 „	0·002 „	÷ 0·007 „	÷ 0·22
FeO	0·078 „	0·056 „	÷ 0·022 „	÷ 0·68
CrO	0·002 „	—	÷ 0·002 „	÷ 0·05
MgO ...	1·780 „	1·065 „	÷ 0·715 „	÷ 22·20
Water ..	0·006 „	0·336 „	+ 0·330 „	+ 10·25
	3·220 „	2·530 „		

The transformation of olivine into serpentine can take place therefore only by loss of a portion of each of its constituents and assumption of water.

It is interesting to compare the chemical constitution of the minerals occurring with serpentine with the constituents separated in the above transformation. The following minerals, in addition to olivine, are found on the serpentine bed; talcspar or magnesite, hydrotalcite, quartz, mica, magnetic iron ore, and titaniferous iron: these, as pointed out by G. Rose, are probably products of the decomposition. The greater part of the magnesia separated in the transformation above described, is found in the talcspar, this mineral having been formed by the combination of the carbonic acid of the waters which decomposed the olivine, with the magnesia and a small quantity of iron oxide. Another portion of magnesia, by combining with the alumina and with water, has formed hydrotalcite. The separated constituents, together with the alkalis of the water, may have formed a mica, and the separated silica and ferrous oxide may have furnished material for the quartz and magnetic iron oxide. No titanic acid has been found in the olivine: but it is not improbable that the titaniferous iron may have pre-existed in the original olivine, as its mode of occurrence seems to show that it is older than the hydrotalcite, which indeed often forms a crust round the titaniferous iron.

H. W.

Buchonite, a Rock belonging to the Nephelenite Group.
By F. SANDBERGER (Münch. Akad. Ber., 1872, 203—208).

THIS rock occurs on the Calvarienberg, near Poppenhausen, on the Steinberg, near Sinsheim in Baden, and in other localities, usually

as a dark grey, fine-grained mass, in which are embedded very thin laminæ of a micaceous mineral, giving to the whole the appearance of porphyry. Examination with a lens shows also white substances, some of which have a fatty lustre; black, highly lustrous hornblendes; and magnetic iron ore, often in well-developed octohedrons. In other very fine-grained portions which have undergone alteration and have a blue-black colour, the same minerals are seen only after etching with acid, or in microscopic sections; then, however, augite and triclinic felspars also come to light, but in much smaller crystals than the mica and hornblende. All the sections likewise exhibit hexagonal and needle-shaped crystals, mostly embedded in the mica, which give the reactions of phosphoric acid, and doubtless consist of apatite.

In the variety from Poppenhausen, and less frequently in that from Sinsheim, there occur coarse-grained masses free from magnetic iron ore, but containing hornblende in long prisms or radiating tufts of a raven-black colour; nepheline having a faint fatty lustre; orthoclase and mica; occasionally also apatite and plagioclase; chrysolite occurs sparingly in the Poppenhausen variety, more abundantly in that from Sinsheim. The mica forms black-brown hexagonal tables having almost a vitreous lustre; it contains large quantities of ferrous and ferric oxides, but little alumina and magnesia, and much potash.

Buchonite is distinguished from nephelinite by the abundant and constant occurrence of hornblende, and of a mica which is not identical with biotite (true magnesia mica). Only the variety from Sinsheim has yet been analysed quantitatively, namely, by C. Gmelin (*Leonhard's Beiträge*, i, 85), who found it to be composed as follows:—

a. Gelatinising portion; *b.* Non-gelatinising portion; *c.* Total constituents, according to Roth's calculation.

	SiO_2.	Al_2O_3.	FeO.	MgO.	CaO.	K_2O.	Na_2O.	H_2O.	
a..	35·91	13·45	28·98	3·13	4·02	2·41	5·34	1·23	= 99·47
b..	63·82	12·95	14·68	4·13	4·14	—	—	—	= 99·72
c..	51·42	15·39	21·04	3·68	4·09	1·07	2·37	0·55	= 99·61

Phosphoric acid, chlorine, and titanic acid were not determined.

The gelatinising is to the non-gelatinising portion in the proportion of about 3 : 4.

The analysis is sufficient to show the difference between buchonite and the nephelinite of the neighbouring Katzenbuckel, this difference being most conspicuous in the amounts of iron and alkali.

H. W.

The Composition of Guanos, their Alterations, and the probable Origin of the Fossil Phosphates of the Lot District. By A. BAUDRIMONT (Compt. rend., lxxvi, 645).

CONCRETIONS of nodules are often met with in Peruvian and Bolivian guanos, which, after washing, consist almost entirely of calcic phosphate, and resemble very closely the phosphates of the Lot district, with the exception of being rather more porous. The author thinks that the phosphates from this district are, by their origin, guanos, the ferric

phosphate and calcic carbonate, &c., which they contain, having been introduced by the infiltration of water containing either these substances, or others which, by double decomposition, have produced them. These phosphates and those from Sombrero do not contain fluorine, which is always present in Estramadura apatite.

E. K.

On a Mass of Meteoric Iron from Cape Colony.

By L. Smith (Compt. rend., lxxv, 294—297).

This mass, the fall of which was seen by a Dutch farmer at Victoria West, Cape Colony, in 1862, originally weighed 3·25 kilograms, and was pear-shaped, the larger end being smooth and rounded, the smaller end rough, as if the mass had been detached from a larger meteorite. The author has examined a portion of the mass, weighing 375 grams. It is compact, and shows at certain points on its surface a tendency to crack. The exterior is slightly oxidised, but fresh sections present a brilliant metallic appearance throughout. When treated with acids, the iron exhibits the figures of Widmannstadt, of the form often seen in meteoric iron rich in schreibersite, which mineral is, in fact, disseminated through the meteorite in small masses bounded by straight lines, some of which are 10—19 millimeters long and 3 broad, whilst others are triangular or arrow-shaped. The meteorite contains also a kidney-shaped mass of pyrites, 38 millimeters long and 25 broad, enveloped in a coating of schreibersite about 1 millimeter thick. The density of the meteorite is 7·692. Analysis gave the following numbers :—

Iron.	Nickel.	Cobalt.	Copper.	Phosphorus.	
88·83	10·14	0·53	trace	0·28	= 99·78

J. R.

Organic Chemistry.

Application of Concentrated Ozone in Organic Chemistry, Ozobenzene. By A. Houzeau and A. Renard (Compt. rend., lxxvi, 572—574).

By the action of ozone on pure benzene, formic, acetic, and other undetermined acids are produced, together with a peculiar substance to which the authors give the name *ozobenzene.*

It is a white gelatinous body, which explodes violently when struck or heated. It undergoes rapid spontaneous decomposition.

Ethylene, mixed with strongly ozonised oxygen, explodes violently.

Concentrated ozone seems to have no action on methane at ordinary temperatures.

W. A. T.

Nitro-Compounds of the Fatty Series. V.

By V. Meyer and C. Wurster (Deut. Chem. Ges. Ber., vi, 94—96).

The product obtained by the action of bromine on sodium nitro-ethane (this Journal [2], xi, 261), is a mixture of nitro-ethane, monobromonitro-ethane, and dibromonitro-ethane.

Monobromonitro-ethane, $CH_3—CHBr(NO_2)$, can be obtained nearly pure by a long-continued fractional distillation. It is a very heavy oil, smelling like chloropicrin, and boiling at 145°—148°. It dissolves in strong aqueous potash or ammonia, with evolution of heat, and yields crystalline compounds with a concentrated soda-solution and alcoholic ammonia. These salts, however, always contain some metallic bromide and for this reason it is impossible to purify the crude monobromonitro-ethane by dissolving it in alkalis and precipitating it with acids, the product thus formed having a less constant boiling point than the original substance, and leaving on distillation a residue, which decomposes with deflagration and formation of a dense black smoke.

Dibromonitro-ethane, $CH_3—CBr_2(NO_2)$, has no acid properties, and can easily be obtained pure by treating the higher boiling fraction with potash. It is a limpid, mobile liquid, having the same pungent smell as the monobromo-compound, and boiling at 162°—164°.

C. S.

On a Compound of Sugar and Potassium Chloride.

By Ch. Viollette (Compt. rend., lxxvi, 485).

The author has obtained the compound $C_{12}H_{20}KClO_{11}$, in permanent crystals sufficiently large for measurement. He finds it to be isomorphous with sugar.

J. R.

Dextrin. By C. Barfoed (J. pr. Chem. [2], vi, 334—342).

The author's researches show that pure dextrin undergoes alcoholic fermentation by the action of yeast alone. The fermentation takes place much more slowly than that of sugar; increase of temperature hastens the action considerably. In this process the dextrin is seemingly converted directly into alcohol without previous formation of grape-sugar. Carbon dioxide is the only gaseous product of the reaction.

The author states that 200 c.c. of a solution of one part crystallised neutral copper acetate in 15 parts water, to which are added 5 c.c. of acetic acid (containing 38 per cent. true acid), when heated with dextrin, is not reduced; but that if even $\frac{1}{10}$ per cent. of grape-sugar be present, cuprous oxide is precipitated on boiling the liquid and leaving it at rest. This reaction was used by the author to test the purity of the dextrin employed in his experiments.

M. M. P. M.

The Sucrocarbonates of Lime. By P. Horsin-Déon (Bull. Soc. Chim. [2], xix, 65—72).

It is well known that when a current of carbonic acid is passed into a solution of one of the sucrates of lime either alone or mixed with a moderate excess of sugar, the gas is at first absorbed without the production of any precipitate. But in operating at a sufficiently high density, according to the composition of the sucrate, the whole mass at a certain stage suddenly becomes converted into a jelly; by continued passage of the gas, this jelly is destroyed, the whole of the lime being precipitated as carbonate, and sugar being left in solution. If the magma, made in the cold be heated, a certain portion of calcium carbonate is thrown down, and a calcium sucrate containing an excess of sugar left.

M. Horsin-Déon adduces his reasons for considering that a great number of distinct and definite compounds are formed under the varying conditions of concentration, proportion of lime to sugar, temperature, &c., but does not quote any experiments on which his conclusions are founded. The equations contained in the paper are somewhat confusing, since the two sides do not always agree, and consequently an abstract of the body of the paper, as it stands, would convey no idea of the author's meaning.

C. H. G.

Action of Fuming Nitric Acid on Acetochlorhydrose. By A. Colley (Compt. rend., lxxvi, 436—438).

Acetochlorhydrose, a body formed by the action of chloride of acetyl on glucose, offers, by reason of its greater stability, an easier means of obtaining other derivatives of glucose than glucose itself. By submitting this body to the action of nitric acid, the author has obtained a crystalline compound which he calls *acetonitrose*. This substance is prepared by dissolving acetochlorhydrose in 15 to 20 parts of fuming nitric acid, both being previously cooled to 0°, and after two or three hours pouring the solution into ice-cold water. The white flocculent precipitate thereby formed collects in the form of a heavy fine powder, consisting of acetonitrose and unaltered acetochlorhydrose. After drying in a vacuum, the product is purified by crystallisation from ether or alcohol.

Acetonitrose crystallises in oblique prisms or large rhombic tables. It is insoluble in water and tasteless. It burns brilliantly when heated on platinum foil, but does not explode either by heat or by percussion. It fuses at 145° without decomposition. Its sp. gr. at 18° is 1·3487. It rotates a ray of polarised light to the right; $[\alpha]\,j = 159°$. When heated to 100° with water or alcohol in close vessels, it undergoes decomposition, yielding a body which reduces cupropotassic tartrate, and is blackened by alkalis. Its formula deduced from analysis is $C_6H_7O(C_2H_3O_2)_4NO_3$, which is that of acetochlorhydrose in which the chlorine is replaced by the group NO_3. This formula is confirmed by the fact that the substance evolves ammonia when submitted to the action of nascent hydrogen, showing that it is an ether of nitric acid, and not a nitro-substitution product.

J. R.

The Preparation of Acetic Acid. By F. Mohr (N. Repert. Pharm., xxii, 28—32).

The author's statement that one equivalent of sulphuric acid is sufficient for the decomposition of sodium acetate has been called in question by Hager, who states that, for the complete separation of the acetic acid at its own boiling point, two equivalents of sulphuric acid are required; and he also states that when only one equivalent of sulphuric acid is employed, the temperature required is so high that a portion of the sulphuric acid is reduced to sulphurous acid, and an empyreumatic odour is communicated to the product.

The author has now repeated his previous experiments, and finds that by distilling sodium acetate with one equivalent of sulphuric acid, 95·9 per cent. of the theoretical amount of acetic acid is obtained in the pure state, perfectly free from sulphurous acid.

Moreover, acetic acid may be obtained by distilling a mixture of potassinm bisulphate and sodium acetate, and glauber salt is not decomposed when acetic acid is distilled from it.

T. B.

The Preparation of Acetic Acid. By L. A. Buchner (N. Repert. Pharm., xxii, 32—35).

At the request of Dr. Mohr the author has investigated the decomposition of sodium acetate by sulphuric acid, and he finds that one equivalent of sulphuric acid is sufficient for the decomposition of the salt. The acetic acid obtained was quite free from empyreumatic odour and sulphurous acid, but it contained a trace of sulphuric acid which doubtless arose from a slight bumping which took place at the commencement of the distillation.

A quantity of sodium acetate was treated with 1 equivalent of sulphuric acid, and the mixture was allowed to remain in a warm place until all the acetic acid had volatilised, when the residue was found to consist of sodium sulphate without a trace of acetate.

T. B.

On the Freezing-points of Mixtures of Acetic Acid and Water. By E. Grimaux (Compt. rend., lxxvi, 486—489).

The addition of water to glacial acetic acid lowers the freezing-point down to a certain limit, beyond which the further addition of water raises it. The author has endeavoured to ascertain this limit by experiment. He introduced mixtures of acetic acid and water (in proportions determined by weighing) into a small test tube furnished with an alcohol thermometer, the zero-point of which was verified every day, and placed the arrangement in a freezing-mixture. When the thermometer had sunk some degrees below the expected freezing-point of the mixture, the test-tube was shaken to cause solidification of its contents, and the highest point to which the thermometer rose at the moment of crystallisation was read off. The standard acetic acid employed solidified at 14·4°, and hence, according to Rüdorff's

tables, contained 1·25 p.c. of water. The following numbers were calculated on this assumption:

Water.	Acetic acid.	Temp. observed, *mean.*	Water.	Acetic acid.	Temp. observed, *mean.*
7·31	92·69	+ 5·4°	49·38	50·62	− 19·8°
13·25	86·75	− 1·4°	56·54	43·46	16·4°
23·52	76·48	11·7°	61·68	38·22	14·5°
31·18	68·82	19·0°	69·23	30·77	10·9°
33·56	66·44	20·5°	76·23	23·77	8·2°
38·14	61·86	24·1°	79·22	20·78	7·2°
44·50	55 50	22·3°	81·89	18·11	6·3°

The lowest temperature, as is seen, corresponds to a mixture containing 37 or 38 p.c. of water, that is, to an acid represented by the formula $C_2H_4O_2 + 2H_2O$.

The temperatures observed are relative rather than absolute: in general, the point of solidification is rather higher than the melting-point. In a comparative experiment with pure water, the freezing-point was found to be 0·8° with a thermometer verified by means of melting ice.

J. R.

Action of Zinc on Acetyl Chloride.

By D. Tommasi and G. Quesneville (Compt. rend., lxxvi, 496).

Gerhardt obtained by this reaction a brown amorphous product, together with zinc chloride; the authors have obtained a body which they term *acetylide*, its formula being $C_{16}H_{18}O_4$; it may be purified by evaporating off the excess of acetyl chloride, dissolving the residue in alcohol, and precipitating with water, the process being repeated several times. It is soluble in alcohol, ether, hydrochloric acid, fuming nitric acid, acetic anhydride, and chloroform; it does not reduce cupropotassic tartrate: bromine combines with it.

The authors consider that this body is formed, together with water and acetic acid, by the reaction—

$$5\begin{matrix}C_2H_3O.Cl\\C_2H_3O.Cl\end{matrix} + 5Zn = 5ZnCl_2 + 2H_2O + 2C_2H_4O_2 + C_{16}H_{18}O_4.$$

and attribute to it the structure—

$$2(C_2H_3O—C_2H_2—C_2H_2—C_2H_2—O.)$$

C. R. A. W.

Production of Propionic Acid by means of Carbon Oxide.

By M. Berthelot (Bull. Soc. Chim. [2], xix, 160).

Referring to a recent paper of Hagemann's on this subject (*Chem. Soc. Journ.* [2], ix, 143), Berthelot points out that the results arrived at by the author were the same as he had himself previously made known.

J. R.

Propionic Acid. By Is. Pierre and E. Puchot (Ann. Chim. Phys. [4], xxviii, 71—86).

After a quantity of the propyl alcohol which is produced during fermentation had been prepared in the pure state, the propionic acid resulting from its oxidation was subjected to examination.

When powdered potassium dichromate is added gradually to a mixture of water, sulphuric acid and propyl alcohol, the principal product is propylic propionate, this being readily decomposed by caustic potash into propyl alcohol and propionic acid. The authors prefer to prepare propionic acid by gradually adding a mixture of propyl alcohol, water, and sulphuric acid to a solution of potassium dichromate to which sulphuric acid has been added. The reaction being terminated, the mixture yields dilute propionic acid on distillation. In order to obtain the acid in a concentrated form, its potassium salt is treated with sulphuric acid diluted with a small quantity of water, the whole being kept for some time at a temperature of about 80°, when the propionic acid separates as a yellowish liquid which may be decanted from the saline residue. The crude acid thus obtained, crystallises on cooling, but after distillation it no longer possesses the property of crystallising at the ordinary temperature, the crystallisation being apparently facilitated by the presence of a small quantity of potassium bisulphate. The acid thus obtained yields on fractionation the acid $C_3H_6O_2$ (called by the authors the monohydrate, $C_6H_5O_3HO$) in the pure state. It boils at 141·5 under a pressure of 760 mm., and possesses an odour recalling that of glacial acetic acid and that of pure butyric acid. Its specific gravity is 1·0143 at 0°, 0·9607 at 49·6°, and 0·9062 at 99·8°. From these data a table has been constructed which gives the specific gravity for each 10° between 0° and 140°, and also shows its volume at each of the given temperatures.

The barium salt may be obtained in large crystals by allowing its solution to evaporate spontaneously, or as a granular powder consisting of small crystals by cooling a hot solution. The crystals dried by the heat of the sun were found to retain one molecule of water $2(C_3H_5O_2)Ba.H_2O$.

The silver salt was obtained by double decomposition between barium propionate and silver sulphate. It crystallises from water in masses of fine silky needles containing no water of crystallisation. During solution in water, the crystals execute gyratory movements.

T. B.

New Researches on Butyric Acid. By Is. Pierre and E. Puchot (Ann. Chim. Phys. [4], xxviii, 363—382).

The authors being in possession of a large quantity of pure butylic alcohol of fermentation, have prepared butyric (isobutyric) acid from it by oxidation with chromic acid mixture, with the view of reconciling what they regard as the discrepant statements of former observers regarding its physical properties and those of its derivatives.

By oxidising the alcohol with potassium dichromate and dilute sulphuric acid, they obtained a product consisting chiefly of butylic

butyrate: this was converted by treatment with potash into potassium butyrate; and this salt distilled with dilute sulphuric acid yielded aqueous butyric acid, from which, by a series of fractional distillations, pure butyric acid was obtained. The acid thus prepared boiled at 155·5° under a pressure of 760 mm., and had a density of 0·9697 at 0°, 0·916 at 52·6°, 0·8665 at 99·8°, and 0·822 at 139·8°, agreeing in fact exactly with the isobutyric acid obtained by Morkownikoff, whose experiments published in 1865, the authors do not mention. The ethylic butyrate prepared by Pierre and Puchot likewise agrees very nearly in its physical properties with that obtained in like manner by Morkownikoff.

Normal butyric acid prepared either by oxidation of normal butyl alcohol or by the fermentation of sugar in contact with putrid curd, boils at a much higher temperature, viz., at about 164°, and has likewise a higher specific gravity, as determined many years ago by Pelouze and Gélis, by Favre and Silbermann, and by Pierre.

Nevertheless, the authors do not appear to consider the existence of two modifications of butyric acid as distinctly proved (see p. 379 of their memoir); and as their acid agrees nearly in physical properties with the butyric acid obtained by fermentation of sugar, which was examined several years ago by Kopp and by Delffs, and found to boil at 156°, they appear to regard this latter as the pure butyric acid, and the acid of higher boiling point obtained in the same manner, as an impure product. As, however, the butyric acid of fermentation boiling at 164° agrees in its properties and those of its derivatives with the acid obtained by oxidation of normal butylic alcohol, it is more probable that the fermentation acid boiling at 156° examined by Kopp and Delffs was an impure product contaminated with lower homologues, unless indeed it should be found by further investigation that isobutyric as well as normal butyric acid, can be formed by the fermentation of sugar.

The authors also compare the physical properties of their butyric acid with those of the normal butyric acid and isobutyric acid described by Grünzweig (p. 375 of this volume), who found that the normal acid boils at 157°—160° under a pressure of 716 mm., and the iso-acid at 149°—151° under a pressure of 718 mm. Now Pierre and Puchot's acid boiled at 155·5°, and they regard it as a somewhat remarkable circumstance that butyric acid prepared with all possible care from pure materials should boil at a temperature about half way between the boiling points of normal and isobutyric acid as given by Grünzweig. But they omit to notice that the boiling point of their own acid is given for the pressure of 760 mm. at which the boiling point of the normal acid, as determined by several observers, is 164°, and that of the iso-acid about 155°.

The results given in the authors' paper are very valuable as exact determinations of carefully prepared isobutyric acid and its derivatives; but their doubts as to the existence of two isomeric butyric acids will not perhaps be considered to have much weight in comparison with the positive results obtained by other chemists.

H. W.

Œnanthylic Acid. By C. SCHORLEMMER (Deut. Chem. Ges. Ber., vi, 58—59).

THE author obtained from normal heptane a heptylic acid which he found to be identical with the œnanthylic acid from castor-oil. Franchimont, who has also examined a heptylic acid which he obtained from primary heptyl alcohol, and which he regards as a normal compound, thinks that the identity of these two acids has not been sufficiently established. He says that on oxidising castor-oil with nitric acid, a whole series of acids is formed, amongst which Tilley found also caproic acid, and thus it is possible to obtain a mixture (corresponding to butyro-acetic acid), having the composition of a heptylic acid. To this the author replies that he did not prepare his acid in so crude a way, but obtained it by oxidising pure œnanthol with potassium dichromate and dilute sulphuric acid. The œnanthylic acid thus produced, has the same boiling point and smell as the acid from heptane, and both yield barium salts having the same composition and crystalline form.

When crude œnanthol is employed for the preparation of œnanthylic acid, a mixture of acids is obtained; but it is easy to isolate from it pure œnanthylic acid, which boils at 222°—224° (corrected), solidifies at −10·5° to a crystalline mass consisting of pointed plates or needles, and melts again at the same temperature. The heptylic acid from heptane does not solidify in a freezing mixture.*

C. S.

On the Sulpho-carbonic Ethers.
By F. SALOMON (J. pr. Chem. [2], vi, 433—453).

BY the action of ethyl chloro-carbonate on an ethereal solution of sodium mercaptide, the author has obtained a new ethyl mono-sulphocarbonate, as a colourless, highly-refractive liquid, which boils at 156°. It possesses a peculiar odour of rotten fruit, and an aromatic taste. It is inflammable, insoluble in water, but easily soluble in alcohol and ordinary ether. Sp. grav. at 18° = 1·0285.

The following equation represents its formation:—

$$CO\left\{\begin{matrix}OC_2H_5\\Cl\end{matrix}\right. + C_2H_5SNa = CO\left\{\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}\right. + NaCl.$$

This view of its constitution is confirmed by the action of potassium hydrate upon it.

$$CO\left\{\begin{matrix}OC_2H_5\\SC_2H_5\end{matrix}\right. + 2KHO = \underset{\text{Potassium carbonate.}}{CO\left\{\begin{matrix}OK\\OK\end{matrix}\right.} + \underset{\text{Mercaptan.}}{C_2H_5SH} + \underset{\text{Alcohol.}}{C_2H_5OH.}$$

* The abstractor, in conjunction with Mr. Grimshaw, is at present engaged in a further investigation of these acids. The results which they have so far obtained make it highly probable that Franchimont's acid is identical with œnanthylic acid, and with the acid from heptane. That the latter does not solidify at −10·5° is not surprising, for it obviously contains traces of other acids, and it is well known that the freezing-point of a fatty acid is much lowered by such an admixture.—C. S.

Ammonia also reacts with the ether, giving rise to urethane and mercaptan.

$$CO\begin{cases}OC_2H_5\\SC_2H_5\end{cases} + NH_3 = \underset{\text{Urethane.}}{CO\begin{cases}OC_2H_5\\NH_2\end{cases}} + \underset{\text{Mercaptan.}}{C_2H_5SH.}$$

Water at 160° decomposes it into CO_2, mercaptan and alcohol.

The author has also prepared the same compound by the action of ethyl bromide upon the salt $CO\begin{cases}OC_2H_5\\SK\end{cases}$ which is formed by the action of potassium ethylate on ethyl xanthate, and possesses the constitution indicated by this formula.

The discovery of the new ethyl mono-sulphocarbonate completes the series of possible ethylic sulphocarbonates.

The author gives the following summary of their history and reactions:—

I. *Carbonyl oxysulphodiethyl*, $CO\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix}$.—1. By treating sodium mercaptide with ethyl chlorocarbonate (Salomon).

2. By decomposing the compound, $CO\begin{smallmatrix}OC_2H_5\\SK\end{smallmatrix}$ with ethyl bromide (Salomon).

II. *Sulphocarbonyl-dioxydiethyl*, $CS\begin{cases}OC_2H_5\\OC_2H_5\end{cases}$.—By decomposition of ethyl-disulphocarbonic sulphide by heat (Debus).

III. *Carbonyl-disulpho-diethyl*, $CO\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix}$.—1. By the action of sulphuric acid on ethyl sulphocyanate (Schmitt and Glutz).

2. By acting on sodium mercaptide with phosgene gas (Salomon).

IV. *Sulphocarbonyl-oxysulpho-diethyl*, $CS\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix}$.—1. By action of ethyl iodide, bromide, or chloride on potassium xanthate (Debus; Salomon).

2. By heating ethyldisulphocarbonic sulphide (Debus).

V. *Sulphocarbonyl-disulpho-diethyl*, or *diethylic trisulphocarbonate*, $CS\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix}$.—By treating potassium trisulpho-carbonate with ethyl chloride, bromide, or iodide (Schweitzer; Husemann).

Behaviour of the Ethers with Potassium Hydrate.

$$\underset{\substack{\text{Carbonyl dioxydiethyl, or}\\\text{diethylic carbonate.}}}{CO\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}} + 2KOH = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{CO\begin{smallmatrix}OK\\OK\end{smallmatrix}} + \underset{\text{Alcohol.}}{2C_2H_5OH.}$$

$$\text{I. }\underset{\substack{\text{Carbonyl oxysulpho-}\\\text{diethyl.}}}{CO\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix}} + 2KOH = \underset{\substack{\text{Potassium}\\\text{carbonate.}}}{CO\begin{smallmatrix}OK\\OK\end{smallmatrix}} + \underset{\text{Alcohol.}}{C_2H_5OH} + \underset{\text{Mercaptan.}}{C_2H_5SH.}$$

$$\text{II. } CS^{OC_2H_5}_{OC_2H_5} + KOH = CO^{OC_2H_5}_{SK} + C_2H_5OH.$$

Sulphocarbonyl dioxydiethyl. — Potassic carbonyl oxethyl sulphide. — Alcohol.

$$\text{III. } CO^{SC_2H_5}_{SC_2H_5} + 2KOH = CO^{OK}_{OK} + 2C_2H_5SH.$$

Carbonyl disulphodiethyl. — Potassium carbonate. — Mercaptan.

$$\text{IV. } CS^{OC_2H_5}_{SC_2H_5} + KOH = CO^{OC_2H_5}_{SK} + C_2H_5SH.$$

Sulphocarbonyl oxysulphodiethyl. — Potassic carbonyl oxethyl sulphide. — Mercaptan.

$$\text{V. } CS^{SC_2H_5}_{SC_2H_5} + KOH + C_2H_5OH = CO^{OC_2H_5}_{SK} + 2C_2H_5SH.$$

Sulphocarbonyl-disulphodiethyl. — Potassic carbonyl oxethyl sulphide. — Mercaptan.

Behaviour of the Ethers with Ammonia.

$$CO^{OC_2H_5}_{OC_2H_5} + 2NH_3 = CO^{NH_2}_{NH_2} + 2C_2H_5OH.$$

Diethylic carbonate. — Urea. — Alcohol.

$$\text{I. } CO^{SC_2H_5}_{OC_2H_5} + NH_3 = CO^{OC_2H_5}_{NH_2} + C_2H_5SH.$$

Carbonyl oxysulpho-diethyl. — Urethane. — Mercaptan.

$$\text{II. } CS^{OC_2H_5}_{OC_2H_5} + 2NH_3 = CSN(NH_4) + 2C_2H_5OH.$$

Sulphocarbonyl-dioxethyl. — Ammonium sulphocyanate. — Alcohol.

$$\text{III. } CO^{SC_2H_5}_{SC_2H_5} + 2NH_3 = CO^{NH_2}_{NH_2} + 2C_2H_5SH.$$

Carbonyl-disulpho-diethyl. — Urea. — Mercaptan.

$$\text{IV. } CS^{OC_2H_5}_{SC_2H_5} + 2NH_3 = CSN(NH_4) + C_2H_5SH + C_2H_5OH.$$

Sulphocarbonyl-oxysulphodiethyl. — Ammonium sulphocyanate. — Mercaptan. — Alcohol.

$$\text{V. } CS^{SC_2H_5}_{SC_2H_5} + 2NH_3 = CSN(NH_4) + 2C_2H_5SH.$$

Sulphocarbonyl-disulphodiethyl. — Ammonium sulphocyanate. — Mercaptan.

Comparison of the Boiling Points.

	B.-P.			
$CO\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$	125°		Diff. 31°.	
$CO\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix}$	156°	Diff. 5°.		Diff. 40°.
$CS\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix}$	161°			Diff. 39°.
$CO\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix}$	196°	Diff. 4°.		
$CS\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix}$	200°		Diff. 40°.	
$CS\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix}$	240°			

1. Hence the introduction of an atom of sulphur into the ethylated radicle is accompanied by a rise of 40°, except in the case of the first two members of the series.

2. The introduction of sulphur into the carbonyl group is attended by a rise of 4°—5° in the boiling point.

Specific Gravities of the Ethers at 19°.

$$CO\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} = \cdot 975$$

$$CO\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix} = 1\cdot 0285$$

$$CS\begin{smallmatrix}OC_2H_5\\OC_2H_5\end{smallmatrix} = 1\cdot 0325\,?$$

$$CO\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix} = 1\cdot 085$$

$$CS\begin{smallmatrix}OC_2H_5\\SC_2H_5\end{smallmatrix} = 1\cdot 085$$

$$CS\begin{smallmatrix}SC_2H_5\\SC_2H_5\end{smallmatrix} = 1\cdot 152$$

W. A. T.

Indices of Refraction of the Sulphuretted Substitution Derivatives of the Carbonic Ethers. By E. WIEDEMANN (J. pr. Chem. [2], vi, 453—455).

THESE bodies, which have been recently examined by Salomon, are divisible into two classes containing respectively the radicles CO and CS.

The author finds that the replacement of O by S in these bodies is

accompanied by an increase in the refractive index of the liquid, and that in comparing any two which are isomeric with each other, the index of the one which contains CS is greater than that of the other which contains CO. It is further to be remarked that there is an increase in the index when, outside the radicle CO, there is a replacement of oxygen first by one and then by a second atom of sulphur. In the latter case, the increase is greater than in the former.

W. A. T.

Action of Bromine on Dibromosuccinic Acid.

By E. BOURGOIN (Bull. Soc. Chim. [2], xix, 148—152).

WITH the view of obtaining tribromosuccinic acid, the author heated mixtures of bromine and dibromosuccinic acid with water, in sealed tubes, to various temperatures. The results of the experiments varied, but in no case was tribromosuccinic acid obtained in any considerable quantity, and the reaction was always attended with formation of gas, consisting of hydrobromic acid, carbon oxide, and carbon dioxide, in varying proportions. The most satisfactory result was obtained by heating 1 mol. of dibromosuccinic acid with 4 mol. of bromine and water to 190°. The gas which escaped on opening the tube contained 96·55 p.c. carbon dioxide, and 3·45 carbon oxide, with a trace of hydrobromic acid. The chief product of the reaction was a dense liquid which, on distillation, was found to consist mainly of a colourless liquid boiling at 206°, and having a strong aromatic odour and a warm, sweet taste, resembling that of chloroform. Analysis of this liquid led to the formula $C_2H_2Br_4$, and its formation corresponds with the following decomposition of tetrabromosuccinic acid:—

$$C_4H_2Br_4O_4 = 2CO_2 + C_2H_2Br_4.$$

Whether this body is tetrabromide of acetylene or dibromide of dibromethylene remains to be seen.

The author points out that the production from succinic acid of a body containing 2 atoms of carbon, under the above circumstances, is analogous to the production of ethylene by the electrolysis of the same acid.

J. R.

Mucic Acid and Pyromucic Acid. By H. LIMPRICHT

(Ann. Chem. Pharm., clxv, 253—302).

THE following investigation has been carried out during the last five years by Professor Limpricht and his pupils. The mucic acid was obtained together with oxalic acid, by oxidising sugar of milk with nitric acid. The normal ether, $C_6H_8O_8(C_2H_5)_2$, is not formed by the action of hydrochloric acid or sulphuric acid on a mixture of mucic acid and alcohol, and can only be obtained by Malaguti's method; *i.e.*, by heating mucic acid with sulphuric acid until the mass blackens, and adding alcohol to it after 12 hours' standing.

The crystalline product is again allowed to stand for 24 hours, then washed with cold alcohol, and recrystallised from hot alcohol; it melts

at 158°. By boiling it with water it is decomposed, mucic acid separating out. Hot alcohol also decomposes it partially, with formation of the acid ether, $C_6H_9O_8(C_2H_5)$, which remains in the mother-liquor. It crystallises in white silky needles containing 3 mol. of water, and is readily soluble in alcohol and water; at 100° the water escapes, and the ether melts to a glassy hygroscopic mass. When the normal ether is carefully heated in a retort, alcohol distils over, and an amber-coloured mass is left behind, which is readily soluble in water, the solution containing mucic acid. On heating it gradually to 240°, the distillate contains water, alcohol, pyromucic acid, and a volatile crystalline substance, which is insoluble in hot water. The residue forms a black humus-like mass dissolving in alkalis.

Chloromuconic Acid, $C_6H_4Cl_2O_4$.—This acid, which was discovered by Liès-Bodart, and afterwards investigated by Bode and Wichelhaus, is obtained by heating mucic acid with phosphorus pentachloride and decomposing the product with water. It forms long white needles, dissolving readily in alcohol and ether, and in 19 parts of boiling water, but only very sparingly in cold water; it is a bibasic acid. When it is heated, a small quantity sublimes, but the greater part undergoes decomposition. Bromine does not act on it in presence of water at a gentle heat, but by heating the substances in closed tubes, a great quantity of carbon dioxide is formed, together with a crystalline compound and an oily liquid smelling like pepper. Alcoholic potash acts but slowly on the acid; below 190°, a large quantity remains unaltered, whilst above 200° a most violent explosion takes place. By keeping the temperature between these limits, the acid is resolved into hydrochloric acid, acetic acid, and oxalic acid:—

$$C_6H_4Cl_2O_4 + 4H_2O = 2HCl + 2C_2H_4O_2 + C_2H_2O_4.$$

Hydromuconic Acid, $C_6H_8O_4$.—This compound, which has been already described by Bode and Wichelhaus under the name of *muconic acid*, is produced by the action of sodium-amalgam and water on chloromuconic acid. It is a bibasic acid, forming long white needles, melting at 195° and dissolving readily in alcohol and hot water, but only sparingly in cold water.

Adipic acid, $C_6H_{10}O_4$, is readily formed (although neither Bode nor Wichelhaus could obtain it) by adding a little water and a large quantity of sodium-amalgam to hydromuconic acid. It is identical with the acid which Wislicenus obtained by the action of silver dust on β-iodopropionic acid, and Crum-Brown produced by heating mucic acid with hydriodic acid and phosphorus.

Bromhydromuconic acid, $C_6H_7BrO_4 + H_2O$, is formed by dissolving one mol. of hydromuconic acid in hot water and adding one mol. of bromine. It forms white, shining, hard prisms, melting at 183°; it is easily decomposed by heat, and dissolves readily in hot but sparingly in cold water; on evaporating the aqueous solution on a water-bath, hydrobromic acid is given off.

Oxyhydromuconic acid, $C_6H_8O_5$, is produced by adding freshly precipitated silver oxide to an aqueous solution of bromohydromuconic acid. It is readily soluble in water, alcohol, and ether, and crystallises only with difficulty. It volatilizes without decomposition. The barium

salt, $C_6H_6O_5Ba + 2H_2O$, is precipitated from a concentrated aqueous solution by absolute alcohol as a crystalline powder, which at 105° loses a part of the water, becoming $2C_6H_6O_5Ba + H_2O$.

Dibromadipic acid, $C_6H_8Br_2O_4$, is contained in the mother-liquors of bromhydromuconic acid, and obtained in larger quantity by adding bromine to a hot saturated solution of bromhydromuconic acid. It could not be isolated, but its existence was proved by the action of silver oxide on its aqueous solution, by which

Dioxyadipic acid, $C_6H_{10}O_6$, was produced; the acid forms a syrup, and is soluble in alcohol and ether. The barium salt is formed by boiling a solution of dibromadipic acid with baryta-water. It is very soluble in water, and is precipitated by alcohol as a hygroscopic, crystalline powder, $C_6H_8O_6Ba + 4H_2O$, which loses half its water at 150° and begins to decompose at 160°. Its solution is precipitated by silver and lead salts.

Tribromadipic acid, $C_6H_7Br_3O_4$, is produced by adding bromine to a solution of hydromuconic acid heated on a water-bath. A colourless oil, smelling like pepper, separates out, and from the aqueous liquid tribromadipic acid crystallises on standing, in small white needles melting at 177°—180°. By boiling its solution with baryta water the barium salt of trioxyadipic acid is formed, which is very soluble in water and is left on evaporation as an amorphous, transparent mass. Lead- and silver-salts produce with it a white precipitate, and ferric chloride a reddish-yellow precipitate. Alcohol precipitates the barium salt as a light white powder, $4C_6H_8O_7Ba + 3H_2O$, which loses one mol. of water at 85°. The free acid is readily soluble in water and alcohol. By adding alcohol and benzene to a concentrated aqueous solution and allowing to evaporate slowly, it was obtained in prisms. An alcoholic solution turns red on evaporation, without yielding crystals, and an aqueous solution becomes yellowish-brown and colours the skin intensely yellow.

Tetrabromadipic acid, $C_6H_6Br_4O_4$.—A small quantity of this acid was produced by heating one mol. of hydromuconic acid with three mol. of bromine and some water for seven hours to 100°; a large quantity of carbon dioxide and the pungent oil already mentioned were formed at the same time. The acid is sparingly soluble in water, readily in alcohol and ether, and is decomposed when its alcoholic solution is boiled, with formation of a volatile compound having an ethereal smell. It melts at 200°—211° and blackens.

Isodibromadipic acid, $C_6H_8Br_2O_4$, is formed by adding bromine to a warm solution of hydromuconic acid in glacial acetic acid. It is readily soluble in alcohol, ether, and hot water, sparingly in cold water, and crystallises in white warty needles. When heated it melts between 175°—190° and decomposes with ebullition. The barium salt, $C_6H_6Br_2O_4Ba + H_2O$, is an indistinct crystalline mass. When the acid is heated with water and sodium-amalgam it is again reduced to hydromuconic acid.

Muconic acid, $C_6H_6O_4$, is obtained by adding silver-oxide to a hot aqueous solution of isodibromadipic acid and decomposing the silver-salt with hydrochloric acid or hydrogen sulphide. It forms large, apparently monoclinic crystals, melting above 100° and dissolving

freely in water, alcohol, and ether. The *barium salt*, $(C_6H_5O_4)_2Ba + 4H_2O$, forms warty crystals and is freely soluble in water, but not in alcohol. The *sodium salt* forms a syrup; the *ammonium salt* gives a white precipitate with silver nitrate, and its aqueous solution becomes acid on evaporation. When muconic acid is heated for some time to 100°, or a little higher, carbon dioxide is evolved and the residue assumes a dark colour. By boiling the acid with baryta-water it yields carbon dioxide, acetic acid, succinic acid, and another acid which could not be obtained in a pure state.

Pyromucic acid, $C_5H_4O_3$, is produced in a small quantity only by the dry distillation of mucic acid, and is best obtained by the action of alcoholic potash on furfurol. By distilling it with phosphorus pentachloride a mixture of different bodies is formed which could not be separated. When the barium salt, mixed with some soda-lime, is heated, *tetraphenol*, $C_4H_4O_2$, distils over. It is a colourless liquid, having a peculiar smell and boiling at 32°. Tetraphenol is not acted upon by alkalis, and its alcoholic solution is not precipitated by lead- or silver-salts. Sodium and potassium have no action upon it, nor is it changed by passing carbon dioxide into its ethereal solution containing sodium, or by heating it with sodium and carbon dioxide in a closed tube. It does not combine with the bisulphites of the alkali-metals, and remains unaltered when sodium-amalgam is added to its alcoholic solution. Acids act readily on it; concentrated hydrochloric decomposes it with the greatest violence, and dilute acids more slowly, with formation of the so-called *pyrrol-red*—

$$3C_4H_4O - H_2O = C_{12}H_{10}O_2.$$

When two molecules of bromine are added to a solution of one mol. of pyromucic acid, carbon dioxide is evolved, and a very small quantity of an oily liquid separates out. By shaking the aqueous solution with ether, evaporating the ethereal solution on a water-bath, and drying the residue over sulphuric acid, a yellowish syrup is left behind, from which, on standing, white warty crystals having the composition $C_4H_4O_3$, separate out. This body has an acid reaction, and its solution is coloured yellow by excess of alkali. When baryta-water is added until the liquid has only a faint acid reaction, alcohol produces a white precipitate having the composition $(C_4H_3O_3)_2Ba$. An excess of baryta-water produces a yellowish precipitate, the quantity of which increases on heating the solution, which has the same composition. The compound, $C_4H_4O_3$, is also formed by the action of lead oxide or potassium dichromate and dilute sulphuric acid on pyromucic acid; by acting with sodium-amalgam on its aqueous solution, the bodies $C_4H_6O_2$ and $C_8H_{10}O_5$ were formed, and bromine oxidises it to *fumaric acid*, which appears to be also formed by boiling it with water and silver oxide. It seems probable therefore that the compound $C_4H_4O_3$ is the aldehyde of fumaric acid, although it does not combine with the bisulphites of the alkali-metals.

The compound $C_4H_4O_3$ is not always formed by the action of two mol. of bromine on pyromucic acid and water, but several times the body $C_4H_3BrO_3$ was produced, which is formed according to the following equation:

$$C_5H_4O_3 + H_2O + 4Br = C_4H_3BrO_2 + CO_2 + 3HBr.$$

This compound forms white feathery crystals melting at 84°, and smelling like camphor. It readily volatilises with the vapour of water, and is soluble in ether and alcohol, but not in water. Alcoholic potash does not act on it at 180°. By adding sodium-amalgam and sulphuric acid to an alcoholic solution, the compound $C_4H_4O_2$ is formed, a heavy very refractive liquid, smelling like benzene, which is not acted on by hydrochloric acid or by alkalis, and does not combine with alkaline bisulphites.

When an excess of bromine is added to pyromucic acid in presence of water, *mucobromic acid*, $C_4H_2Br_2O_3$, is formed—

$$C_5H_4O_3 + 2H_2O + 8Br = C_4H_2Br_2O_3 + CO_2 + 6HBr.$$

It crystallises in shining white plates, melting at 120°—130°, and dissolves readily in ether, alcohol, and hot water, but only sparingly in cold water.

One mol. of mucobromic acid heated with 3 mol. of bromine and water in closed tubes to 120°—130°, yields *dibromofumaric acid* (?), *tetrabromobutyric acid* (?), *tribromethene dibromide* and *hexbromethane*.

Dibromofumaric acid, $C_4H_2Br_2O_4$, forms warty crystals melting at 108°—120°; on heating it in a current of carbon dioxide to 100°—105°, the anhydride $C_4Br_2O_3$ sublimes in needles, melting at 95°—120°, and volatilising readily at 70°, and at the common temperature *in vacuo*. The anhydride was dissolved in cold baryta-water, and the solution evaporated over sulphuric acid; the salt $C_4Br_2O_4Ba + 2H_2O$ then crystallised in fine plates. The mother-liquor gave with alcohol a crystalline precipitate, $C_4Br_2O_4Ba + H_2O$. The aqueous solution of the barium salt gives with silver nitrate a white explosive precipitate.

Tetrabromobutyric acid, $C_4H_4Br_4O_2$, crystallises from a hot aqueous solution in transparent oblique plates, melting at 115°, and dissolving but sparingly in cold water.

Tribromethene dibromide, C_2HBr_5, crystallises from alcohol in long, brittle needles, melting at 50°—52°; on heating it with alcoholic potash, it was converted into *tetrabromethene*, C_2Br_4, crystallising in thin plates melting at 50°. *Hexbromethane*, C_2Br_6, forms thick colourless prisms which are insoluble in alcohol, and decompose at 170°.

Isopyromucic acid, $C_5H_4O_3$, is produced, together with pyromucic acid, a small quantity of an empyreumatic oil, formic acid, water, carbon dioxide, carbon monoxide, and a gas burning with a luminous flame, by the dry distillation of mucic acid. The operation must be performed in a retort, of which only one-sixth is filled, and heat is applied, first very slowly, so that only one drop passes over every two minutes; afterwards the retort is gradually heated to a dull red-heat. It takes about eight hours to decompose 30 grams of mucic acid. Pyromucic acid decomposes carbonates but slowly, and may therefore easily be separated from the other acids by digesting the distillate with barium carbonate, and shaking the solution with ether. It is readily soluble in water, and sublimes slowly at 100° in a current of carbon dioxide in small thin plates, softening

at 70° and becoming perfectly liquid at 82°. It is a monobasic acid; its aqueous solution is coloured brown by alkalis; baryta-water in excess produces a bulky precipitate, and on boiling the solution becomes intensely red. On adding bromine to its aqueous solution, a yellow crystalline body insoluble in water is formed, together with mucobromic acid.

Furfuryl alcohol, $C_5H_6O_2$, is produced, together with pyromucic acid, by the action of alcoholic potash and furfurol. It is a yellow oil, boiling at about 170°—180°; but the greater part undergoes condensation with elimination of water and formation of resinous bodies, even in an atmosphere of hydrogen or *in vacuo*. Acids convert it into pyrrol-red, and caustic potash acts violently on it, with formation of carbon dioxide, formic acid, acetic acid, and succinic acid.

C. S.

Action of Ammonia on Valeraldehyde. By N. LJUBAWIN (Deut. Chem. Ges. Ber., v, 1101).

WHEN this aldehyde is acted upon by alcoholic ammonia, another base is formed besides valeritrine. The hydrochloride crystallises in needles having the composition $C_{15}H_{29}N.HCl$ or $C_{15}H_{31}N.HCl$, which shows that a part of the aldehyde must have been resolved in amyl alcohol and valerianic acid, and indeed this acid was found amongst the products.

C. S.

Chloral and Acetonitril. By H. HÜBNER (Deut. Chem. Ges. Ber., vi, 109—110).

THE publication of Baeyer's research (*ibid.* v, 1098) on the mutual action of chloral, benzene, and sulphuric acid, by which he obtained a compound $C(C_6H_5)_2HCCl_3$, has caused the author to revise his work done in conjunction with Schreiber (*Zeitschr. f. Chem.* 1871, 712) on the action of chloral on acetonitril. He now finds that the true formula of the crystalline substance then described is $CH(CH_2.CONH_2)_2CCl_3$, and the reaction—

$$\text{I.}\quad \begin{array}{l|c|l} CH_2 & H & .CN \\ CH_2 & H & .CN \\ CH & O & .CCl_3 \end{array} = CH(CH_2.CN)_2CCl_3 + H_2O.$$

$$\text{II.}\quad CH(CH_2.CN)_2CCl_3 + 2H_2O = CH(CH_2.CONH_2)CCl_3.$$

It does not appear unlikely that the isoadipic acid corresponding to this amide, is the substance obtained by Meyer and Dulk (*Deut. Chem. Ges. Ber.*, iv, 963) by the action of chloral on acetic acid. The author intends to investigate this reaction more completely, and also to study the action of chloral on formic acid.

C. E. G.

Action of Potassium Cyanide on Chloral: a New Method for the Preparation of Dichloracetic Acid. By O. Wallach (Deut. Chem. Ges. Ber., vi, 114—119).

On adding one molecule of chloral hydrate to one molecule of potassium cyanide under absolute alcohol, a powerful reaction sets in accompanied by an abundant evolution of hydrocyanic acid. On adding water to the product, a heavy oil separates, from which, by repeated fractional distillation, ethyl dichloracetate boiling between 154° and 157° may be obtained; also, in the higher portion, a solid crystalline substance melting at 62°, and apparently identical with the chloral-cyanhydrate prepared by Pinner and Bischoff, also by Hagemann by the action of hydrocyanic acid and hydrochloric acid on chloral. This compound is very difficult to separate by distillation from the ethyl dichloracetate contained in the intermediate fraction; but by agitating it repeatedly with water, and then distilling in a current of aqueous vapour, the ethyl compound was readily obtained in the pure state. The pure dry ether is stable. On heating it with hydrochloric acid to 150°, it yields ethyl chloride and dichloracetic acid: with alcoholic potash in the cold, it immediately solidifies to a crystalline mass of potassium dichloracetate. The proportion of dichloracetic ether obtained is so considerable, that the author recommends it as the most advantageous method for the preparation of this compound. When the dilute alcoholic solution mentioned above, from which the oil had been separated, is evaporated to dryness at 100°, and exhausted with absolute alcohol, it yields potassium dichloracetate, crystallising from the alcohol in large plates. When potassium cyanide and chloral hydrate react on one another in presence of water, hydrocyanic acid is evolved, and free dichloracetic acid obtained, only a small amount of potassium dichloracetate being produced, and that being probably due to the presence of potassium hydrate or carbonate in the potassium cyanide employed. The reactions which take place may therefore be represented as follows:

$$\text{I. } CCl_3.COH + CNK + H_2O = CCl_2H.COOH + KCl + CNH.$$
$$\text{II. } CCl_2H.COOH + C_2H_6O = H_2O + CCl_2H.COOC_2H_5.$$

When a solution of chloral hydrate in benzene is added to potassium cyanide, the reaction is somewhat different, hydrocyanic acid being evolved, and scarcely anything but chloral-cyanhydrate being formed. On the other hand, if solid chloral-hydrate be added to potassium cyanide under benzene, but little chloral-cyanhydrate is produced, the benzene by spontaneous evaporation leaving microscopic prismatic crystals, melting at 123°, and having the composition expressed by the formula $C_7H_5Cl_6O_2N$. This compound splits up on distillation into chloral and chloralide melting at 112°—114°.

C. E. G.

Conversion of Glycerin into Acetone. By O. Lange (Deut. Chem. Ges. Ber., vi, 98—99).

The product obtained by the action of bromine on dichlorhydrin consists, according to Carius, of dichloro-dibromacetone. By acting on it

with zinc and dilute sulphuric acid, and heating from time to time gently but not above 40°, a slow reaction lasting for several weeks sets in. The product consisted of acetone and a bromine compound (probably isopropyl bromide), which could not be separated by distillation. The presence of acetone was proved by combining it with acid sodium sulphite, and analysing the crystallised compound. The same reduction can be effected by means of hydriodic acid.

C. S.

A Polymeride of Hydrocyanic Acid. By O. LANGE (Deut. Chem. Ges. Ber., vi, 99—101).

WHEN a mixture of equal parts of anhydrous hydrocyanic acid and epichlorhydrin is heated in sealed tubes during a fortnight to 40°—60°, a solid body is formed, which after treatment with ether, and recrystallisation from water and alcohol, is obtained in reddish-brown crystals, the analysis of which does not give concordant results. By the action of baryta-water it yields ammonia, barium carbonate, and a crystalline body having the composition and properties of glycocine. The original substance is therefore probably a polymeride of hydrocyanic acid—

$$C_3H_3N_3 + Ba(OH)_2 + 3H_2O = C_2H_5NO_2 + BaCO_3 + 2NH_3.$$

C. S.

Aspartic Acid Produced in the Oxidation of Conglutin by Potassium Permanganate. By R. POTT (J. fur Chem. [2], vi, 91—95).

THE syrupy mixture of crude products obtained by acting on conglutin with permanganate was dissolved in hot water and shaken up with ether. The part which dissolved in the ether was boiled with hydrated copper oxide, and the salt formed separated by decantation. This salt showed on analysis a percentage composition which induced the author to look upon it as cupric aspartate. In addition to aspartic acid, it is likely that other, probably uncrystallisable amido-acids, are formed by the action of permanganate on conglutin.

G. T. A.

New Derivatives of Sulphocarbamic Acid. By H. HLASIWETZ and J. KACHLER (Ann. Chem. Pharm., clxvi, 137—145).

KETONES and aldehydes form with ammonia and carbon sulphide peculiar crystallised compounds, of which that obtained from common acetone, and consisting of $C_{10}H_{20}N_2S_3$, is best known. The authors tried to obtain a similar compound from camphor, which, as one of them has shown, has a constitution similar to that of the ketones. But camphor does not yield such a compound, the carbon sulphide and ammonia combining together to form a new compound, *which however, curiously enough, is not produced if camphor is absent*, but which is also formed if phenol or benzyl alcohol be substituted for camphor. The new compound is formed according to the following equation:—

$$4NH_3 + 2CS_2 = C_2H_{10}N_4S_3 + H_2S.$$

Its reactions show that it is the ammonium compound of *sulphocarbamic anhydride* or *thiuram-sulphide*,* $S\left\{\begin{matrix}CS.NH_2\\CS.NH_2\end{matrix}\right.$, a compound which is not known in the free state.

Ammonium thiuram-sulphide, $S(CS.NH.NH_4)_2$, is obtained by evaporating a concentrated aqueous solution over potash or quicklime, in beautiful, well-defined, colourless monoclinic crystals; it is a very unstable body, which slowly decomposes even if kept in sealed tubes. When the aqueous solution is boiled with hydrochloric acid, carbon disulphide and hydrogen sulphide are given off, free sulphur separates out, and the solution contains a large quantity of ammonium sulphocyanate. Silver nitrate and lead salts produce yellowish precipitates, which soon blacken. Copper sulphate produces a heavy light-yellow precipitate, consisting of $S(CS.NH)_2Cu$, which is not decomposed by hydrogen sulphide. When a dilute solution of ferric chloride is added to a dilute solution of the ammonium compound containing an excess of hydrochloric acid, the following reaction takes place:—

$$2C_2H_{10}N_4S_3 + Fe_2Cl_6 = C_2H_4N_2S_4 + 2NH_4SCN + 2NH_4Cl + Fe_2Cl_4.$$

Each drop of ferric chloride produces a deep-red colour, which quickly disappears again at first, but remains permanent as soon as the decomposition is complete. The new compound formed is *thiuram-disulphide*, $S_2(CS.NH_2)_2$, it crystallises in shining plates, resembling benzoic acid. On boiling it with water, it undergoes the following decomposition:—

$$C_2H_4N_2S_4 = CS_2 + S + NH_4SCN.$$

Phenylammonium thiuram-sulphide, $S(CS.NH.C_6H_5NH_3)_2$, is readily formed by mixing aniline with carbon sulphide and ammonia; it forms prismatic crystals, and is resolved by boiling water into ammonia, carbon disulphide, and *sulphocarbanilide*, $CS(NH.C_6H_5)_2$.

C. S.

Isuretine, a Base Isomeric with Urea. By W. LOSSEN and P. SCHIFFERDECKER (Ann. Chem. Pharm., clxvi, 295—320).

THE most important results of this research have already been given (*Chem. Soc. J.*, 1872, p. 500). The following additional particulars are gathered from the present paper:—

Isuretine, boiled with dilute sulphuric acid, gives a distillate containing formic acid and a residual solution of ammonia and hydroxylamine salts. This reaction consists in the assimilation of a molecule of water by the isuretine:

$$\underset{\text{Isuretine.}}{N_2CH_4O} + 2H_2O = \underset{\text{Formic acid.}}{CH_2O_2} + \underset{\text{Ammonia.}}{NH_3} + \underset{\text{Hydroxylamine.}}{NH_3O}.$$

An aqueous solution of isuretine, shaken up with benzoyl chloride, deposits a sparingly soluble body, dibenzhydroxamic acid, $NH(C_7H_5O)_2O$. (*Chem. Soc. Journ.*, 1872, 414).

* *Thiuram* is the name given by the authors to the group $NH_2.CS$ (from θεῖον, urea, and ammonium)

No derivative of isuretine is produced under these circumstances; moreover, benzoyl chloride has no action on isuretine in the cold, but on application of heat a violent reaction sets in.

The products of the decomposition of isuretine by water are numerous, the relative proportions in which they make their appearance depending upon the concentration of the solution. When a solution of isuretine in its own weight of water is heated in the water-bath, ammonia, carbonic anhydride, and nitrogen are evolved, and a solution is obtained from which biuret is first deposited, together with a small quantity of a white substance in warty masses.

The mother liquors contain urea, ammonia, guanidine, and another substance apparently uncrystallisable.

The metamorphosis of isuretine into urea presenting a peculiar interest, the authors endeavoured, by special experiments, in which solutions of different degrees of concentration and different temperatures were tried, to find conditions under which isuretine might be wholly converted into urea. In this, however, they were unsuccessful. In the experiment last described, 26 grams of isuretine, heated with an equal weight of water, gave only between two or three grams of urea, and about three grams of biuret. When dilute solutions are employed, very little urea is formed, the base takes up the elements of water, and a solution of ammonium formate is the result, hydroxylamine, which is formed at the same time, being represented only by its products of decomposition, nitrogen, ammonia, and water.

The authors consider isuretine as having the constitution represented by the formula $C\begin{cases}NH\\NH.OH.\\H\end{cases}$

W. A. T.

Decomposition of Neurine. By J. MAUTHNER (Ann. Chem. Pharm., clxvi, 202—207),

WHEN putrid bile is heated on a water-bath, an aqueous solution of ammonia and *trimethylamine* distils over, while fresh bile yields a perfectly neutral distillate. The neurine contained in bile seems therefore to be decomposed by putrefaction, and that this is the case is proved by the following experiments:—

I. The mixture was distilled after standing for ten days—

(*a.*) 100 c.c. of water and 5 c.c. of bile.
(*b.*) 100 c.c. of a solution of neurine (1·4 per cent.) and 5 c.c. of bile.
(*c.*) 100 c c. of water and 5 c.c. of blood.
(*d.*) 100 c.c. of the neurine solution and 5 c.c. of blood.
(*e.*) 100 c.c. of pure neurine solution.

II. Mixture distilled after five days—

(*f.*) 100 c.c. of water and 30 c.c. of bile.
(*g.*) 100 c.c. of neurine solution and 30 c.c. of bile.

III. Distilled after standing for eight days—
- (*h.*) 50 c.c. of a solution of neurine (1·5 per cent.) and 30 c.c. of bile.
- (*i.*) 50 c.c. of water and 30 c.c. of bile.
- (*k.*) 50 c.c. of a solution containing 1·5 per cent. of neurine.

The distillates were passed into standard sulphuric acid and the solution neutralized with standard soda—

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*k.*
c.c. of acid	0·22	0·30	0·15	0 85	0·35	0·30	0·40	0·20	0·20	0·10

From these experiments it appears that neurine is readily decomposed by putrid blood (*d*), the distillate containing a large quantity of trimethylamine, whilst a solution of pure neurine under the same conditions undergoes only a slight decomposition. A very remarkable fact is that, whilst a solution of bile soon becomes quite putrid, the addition of some neurine prevents the putrefaction altogether, the liquid possessing the faint smell of fresh bile even after standing for some weeks. Neurine also prevents the coagulation of albumin and has the property of dissolving fibrin.

C. S.

A New Series of Aromatic Hydrocarbons. By Th. Zincke (Deut. Chem. Ges. Ber., vi, 119—122).

By acting with zinc-dust on a mixture of benzoyl chloride and benzene, products boiling at a very high temperature are formed besides diphenylmethane. The distillate obtained, after the latter body has passed over, is an oily liquid which soon solidifies to a crystalline magma. The solid portion consists chiefly of two isomeric (or perhaps polymeric) hydrocarbons, $C_{20}H_{18}$. One of them crystallises from hot dilute alcohol in large transparent laminæ or oblique plates, melting at 86° and solidifying again at 78°. When slowly cooled it remains amorphous and transparent, but becomes crystalline at once on touching and heating it gently. It is not very soluble in ether, but dissolves readily in benzene, chloroform, and carbon sulphide. The second compound dissolves more readily in ether and the other solvents, and crystallises from hot alcohol in thin, long, flat silky needles, melting at 78° and solidifying at 68°. When cooled down slowly it behaves like its isomeride. Neither of the two combines with picric acid, but the two combine together, crystallising from alcohol in hard, brilliant, acicular prisms, melting at 83°—84°. This compound, or perhaps isomorphous mixture, is not decomposed by recrystallisation from alcohol, and can be resolved in its constituents only by repeated treatment with ether.

C. S.

Action of Zinc on a Mixture of Aromatic Halogen Compounds and Aromatic Hydrocarbons. By T. ZINCKE (Deut. Chem. Ges. Ber., vi, 137).

AN attempt to prepare a body of formula, $C_6H_4\langle{CO \atop CO}\rangle C_6H_4$ (possibly identical with anthraquinone), by acting on benzoyl chloride with zinc did not succeed; no dibenzoyl was formed. When toluene was also present the body $C_6H_5—CO—C_6H_4—CH_3$, which might perhaps have been expected, was not formed; when benzene was employed a small quantity of a body melting at 145°—146°, crystallisable from alcohol, and not volatile at 300°, was produced.

Many aromatic chlorinated bodies act like benzoyl and benzyl chlorides when heated with zinc and a hydrocarbon; chlorobenzol, $C_6H_5CHCl_2$, and benzene should yield triphenyl-methane; phenyl bromacetic acid, $C_6H_5.CHBr.CO.OH$, gives a body of the composition of diphenylacetic acid.

When the action of benzyl chloride on benzene is once started by means of zinc, the metal may be withdrawn without hindering the completion of the reaction whereby diphenyl-methane is produced.

C. R. A. W.

Synthesis of Naphthalene. By B. ARONHEIM (Deut. Chem. Ges. Ber., vi, 67).

THE bromide of the hydrocarbon phenylbutylene, recently described by the author (p. 499 of this volume), is decomposed when distilled over lime heated to dull redness, yielding naphthalene according to the equation—

$$C_{10}H_{12}Br_2 = C_{10}H_8 + H_2 + 2HBr.$$

There is scarcely any carbonisation, and almost the theoretical quantity of naphthalene is obtained.

H. E. A.

Acenaphthene and Naphthalic Acid.

By A. BEHR and W. A. VAN DORP (Deut. Chem. Ges. Ber., vi, 60 – 63).

ACENAPHTHENE was obtained by fractional distillation from the portion of coal-tar boiling between 250°—300°, the fractions distilling between each degrees being collected separately. On allowing the portion boiling from 265°—280° to stand in the cold, hard flat prisms of acenaphthene separated out. Acenaphthene crystallises from hot alcohol in long needles, melting at 94°—96°, and distilling at 267°—269° (not corrected). When boiled for three hours with dilute sulphuric acid and potassium dichromate, it is oxidised to *naphthalic acid*, $C_{10}H_6(CO_2H)_2$, which sublimes in broad serrated plates melting at 266°. Acids precipitate it from an alkaline solution in slender needles melting at the same temperature. The potassium salt, $C_{12}H_6O_4K_2 + 2\frac{1}{2}H_2O$, is precipitated by alcohol in small, pearly plates, and the barium salt, $C_{12}H_6O_4Ba + H_2O$, is a precipitate consisting of small, compact shining

plates. When the acid is heated to 140°—150°, it is converted, without melting, into the anhydride $C_{12}H_6O_3$, and by distilling the calcium salt with slaked lime, pure naphthalene is obtained.

Acenaphthene has been obtained by Berthelot by passing the vapour of ethyl-naphthalene through a red-hot tube. The formation of the bibasic naphthalic acid shows that its constitution is $C_{10}H_6\left\langle\begin{array}{l} CH_2 \\ | \\ CH_2 \end{array}\right.$, the side chains being probably linked to two adjoining carbon-atoms of the naphthalene-nucleus, because naphthalic acid has a great resemblance to phthalic acid.

C. S.

Synthesis of Phenanthrene. By C. GRAEBE (Deut. Chem. Ges. Ber., vi, 125—127).

THIS hydrocarbon is formed, together with toluene, by passing stilbene through a red-hot glass-tube, filled with pieces of glass—

$$3\begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} = 2\begin{array}{l} C_6H_4.CH \\ |\quad\ \ \| \\ C_6H_4.CH \end{array} + 2C_6H_5.CH_3.$$

Phenanthrene is also produced by the same process from dibenzyl, which, as Dreher and Otto have already shown, is first resolved by the action of heat into stilbene and toluene—

$$2\begin{array}{c} C_6H_5.CH_2 \\ | \\ C_6H_5.CH_2 \end{array} = \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + 2(C_6H_5\,CH_3).$$

In one of the experiments, when the temperature rose very high, some anthracene was also formed, being derived from toluene according to Berthelot's synthesis.

C. S.

Constitution of the Chlorophenols, the Nitrophenols and the Chloronitrophenols. By AUG. FAUST (Deut. Chem. Ges. Ber., vi, 132—136).

UP to the present time no direct determination of the position of the nitro-groups in the two isomeric mononitrophenols has been made. Körner's observation that quinone is obtained on oxidation of the amidophenol derived from the non-volatile modification has little value in this respect, since aniline when similarly treated also yields quinone. Schmitt, however, has converted the two nitrophenols into the corresponding chlorophenols by the action of heat on the platinochlorides of their diazo-derivatives: the non-volatile nitrophenol yielding a chlorophenol (b.p. 218°) from which Petersen afterwards obtained hydroquinone by fusion with potash; the volatile modification yielding an isomeric chlorophenol (b.p. 175°—180°) from which the author and Müller have obtained pyrocatechin by fusion with potash.

Körner, and after him Petersen, regard the chlorophenol from non-volatile nitrophenol as a 1 : 2 derivative on account of its conversion into hydroquinone. But it is in no wise proved, says the author, that this is the constitution of hydroquinone; in fact, he considers that the investigation of the corresponding chloro- and nitro-derivatives of phenol renders it more probable that these derivatives belong to the para (1 : 4) series, and that consequently the hydroxyl groups in hydroquinone occupy the positions 1 : 4, and for the following reasons :—

1. The chlorophenol in question (b.p. 218°) yields a single nitro-chlorophenol. If the chlorine occupied any other than the para-position, there would in all likelihood be two isomeric derivatives formed, as is the case with metachlorophenol (1 : 3).

2. Similarly the corresponding (non-volatile) nitrophenol also yields but a single dinitrophenol, whereas metanitrophenol yields two isomeric dinitrophenols.

3. If the groups in non-volatile nitrophenol be assumed to have relatively any other than the 1 : 4 position, it is difficult to explain why, when α-dinitrophenol (m.p. 114°) is chlorinated, the same chlorodinitrophenol (m.p. 110°—111°) is obtained as when the non-volatile nitrophenol is chlorinated, and the resulting nitrochlorophenol further nitrated.

With regard to volatile nitrophenol and the corresponding chlorophenol, the author considers that there is not sufficient evidence to settle whether they are 1 : 2 or 1 : 3 derivatives; he appears, however, rather inclined to regard them as members of the latter series, since he makes the statement that as yet no ortho-derivatives exist among the known chloronitrophenols.

He then discusses the constitution of the various known chloronitrophenols, representing each schematically in the usual manner, and attaching to each the name expressing his view of the constitution. The conclusions arrived at will be evident from the following arrangement :—

Meta-derivatives.	B.-P.	M.-P.	Para-derivatives.	B.-P.	M.-P.
Volatile nitrophenol ..	214°	45°	Non-volatile nitrophenol	—	110°
Chlorophenol........	175·5°—177°	Liquid	Chlorophenol	218°	41°
β-dinitrophenol	—	64°			
Chloronitrophenol....	—	70°			
Dichlorphenol	218°—220°	65°			

Para- and Meta-derivatives.	B.-P.	M.-P.
Paranitrometanitrophenol (α-dinitrophenol)	—	114°
Parachlorometanitrophenol	—	86°—87°
Paranitrometachlorophenol	—	110°
Parachlorometachlorophenol (?)	209°—210°	43°
Parachlorodimetanitrophenol	—	81°
Paranitrometachlorometanitrophenol	—	110°—111°
Paranitrodimetachlorophenol	—	125°
Paranitrodimetanitrophenol (picric acid)	—	120°
Parachlorodimetachlorophenol (trichlorophenol)	236°	67°

H. E. A.

Behaviour of the Quinones when Heated with Soda-lime.
By C. GRAEBE (Deut. Chem. Ges. Ber., vi, 63).

ON distillation of the quinone of the hydrocarbon $C_{14}H_{10}$ (*phenanthrene*), recently examined by the author and by Ostermayer and Fittig (this Journ., xi, 175—177) with soda-lime, an almost theoretical yield of diphenyl is obtained, the decomposition occurring as represented by the equation:—

$$C_{14}H_8O_2 + 4NaOH = C_{12}H_{10} + 2Na_2CO_3 + H_2.$$

Anthraquinone similarly treated gave benzene as main product, together with a relatively very small quantity of diphenyl:—

$$C_{14}H_8O_2 + 4NaOH = 2C_6H_6 + 2Na_2CO_3.$$

Chrysoquinone also yields a hydrocarbon, probably $C_{16}H_{12}$; and a solid body is obtained from pyroquinone, which, however, has not yet been examined.

H. E. A.

Synthesis of Ketones. By S. GRUCAREVIC and V. MERZ
(Deut. Chem. Ges. Ber., vi, 60).

WHEN benzoyl chloride and naphthalene are heated with iron or zinc, *α-naphthylphenyl-ketone* is formed, a crystalline solid melting at 75°. The same compound is produced by heating α-naphthoic acid with benzene and phosphorus pentoxide.

C. S.

New Mode of Synthesis of Acids of the Aromatic Series.
By E. PATERNÒ (Gazzetta chimica italiana, ii, 553).

IT is well known that the compounds of alcohol-radicals of the fatty series can combine directly with the elements of carbonic anhydride, producing saline compounds of acids of the next higher homologous series, and that, by a somewhat similar reaction, the phenols, under the influence of sodium and carbonic anhydride, can be transformed into acids of the salicylic series. Guided by these reactions, and by

the fact that the hydrocarbons of the acetylene series easily form metallic derivatives in which the metal is in direct combination with carbon, the author has submitted acetenyl-benzene, $C_2H(C_6H_5)$, to the joint action of sodium and carbonic anhydride, with the hope of directly introducing the carboxyl group into the hydrocarbon, and thus obtaining an acid, $C_9H_6O_2$, identical with the phenylpropiolic acid which Glaser obtained from cinnamic acid:

$$C_6H_5.C{\equiv}CH + Na + CO_2 = C_6H_5{-}C{\equiv}C{-}COONa + H.$$

Experiment has fully confirmed these anticipations. When a current of dry carbonic anhydride is passed through pure acetenyl-benzene (prepared by dry distillation of barium phenylpropiolate), and small pieces of sodium are introduced from time to time, considerable rise of temperature takes place, and a white saline mass is obtained, which, when dissolved in water, agitated with ether to remove unaltered acetenyl-benzene, and decomposed by hydrochloric acid, yields a precipitate of the new acid, which may be separated from the water by agitation with ether, and is obtained by evaporation in needles having a faint yellow tinge. It may be purified by recrystallisation from boiling water, which on cooling deposits it in long, beautiful needles having a silky lustre. The identity of this acid with Glaser's phenyl-propiolic acid was established by its melting point (134°—137°), and by the fact that it yields by dry distillation a hydrocarbon, which gives, with ammoniacal solution of cuprous chloride, a compound of a fine yellow colour.

Glaser prepared phenyl-propiolic acid by the action of sodium and carbonic anhydride on the brominated oil produced in the transformation of phenyl-dibromopropionic into phenyl-bromolactic acid, which oil, according to Erlenmeyer, is monobromotyrol, and, on account of its transformation into phenyl-propiolic acid, was supposed by Glaser to contain bromacetenyl-benzene. The author's experiments render it probable that the formation of the phenyl-propiolic acid in this reaction was due to the presence of acetenyl-benzene, formed by the action of alcoholic potash on monobromostyrol.

The author proposes to extend his new method of synthesis to other hydrocarbons of the acetylene series, particularly to the compound $CH{\equiv}C{-}CH_2{-}CH_2{-}C{\equiv}CH$, isomeric with benzene, recently discovered by L. Henry; also to examine the action of sodium and carbonic anhydride on the new isomerides of the nitriles discovered by Meyer and Kolbe, and to other compounds of like nature.

H. W.

Action of Sulphocyanates on Benzoic Acid. By A. Kekulé (Deut. Chem. Ges. Ber., vi, 110—114).

The first portion of this communication is a criticism of a paper by Pfankuch (*J. pr. Chem.*, vi, 97), who believed he had obtained benzacrylic acid, $C_6H_5C.COOH$, from the product of the dry distillation of a mixture of baric benzoate and sulphocyanate. Mr. Williams, on repeating the experiment, found that the substance prepared according to Pfankuch's method, was nothing but ordinary benzoic acid, con-

taminated with a mixture of various hydrocarbons, which are left behind on dissolving the acid in ammonia.

Hr. Purpur has also studied the action of benzoic acid on ammonium sulphocyanate. When the two substances are heated together in molecular proportions, the reaction commences at 150°, and is terminated at 170°; carbon oxysulphide, sulphuretted hydrogen, and carbon disulphide are evolved, and a residue is left, consisting principally of benzamide, which can easily be purified by crystallisation; and as the yield is large, amounting to 81 per cent. of the benzoic acid taken, this method can be advantageously employed for the preparation of benzamide.

Letts has shown that when potassium sulphocyanate is distilled with two molecules of benzoic acid, scarcely anything but benzonitril is formed, so that it would seem that the potassium benzoate produced during the reaction abstracts water from the benzamide, forming benzonitril. On making the experiment this was found to be the case. Benzamide distilled with potassium benzoate yields benzonitril. Ammonium benzoate, on the contrary, has no action on benzamide.

C. E. G.

Metanitrobenzoic Acid. By P. GRIESS (Journ. pr. Chem. [2], vi, 384—389).

ABOUT five years ago the author found that the amidobenzoic acid prepared from crude nitrobenzoic acid sometimes contains a small quantity of anthranilic acid, and suspected that this was due to the presence of a new modification of nitrobenzoic acid contained in the crude product. Beilstein and Kuhlberg have since, by oxidising metanitrocinnamic acid, obtained this modification, which they call metanitrobenzoic acid, and the author has now succeeded in isolating it from crude nitrobenzoic acid, which is best prepared by adding an intimate mixture of one part of benzoic acid and two parts of nitre to three parts of sulphuric acid, and heating gently until the nitro-compound swims as an oily layer on the top. The product is boiled three times with twice its weight of water and the boiling solution neutralised with baryta-water. On cooling, barium orthonitrobenzoate crystallises out, and the remainder of it is got rid of by concentrating the mother-liquor and leaving it to stand for some time. On evaporating the filtrate to the consistency of a syrup, the meta-salt is obtained as a crystalline mass, which is purified by recrystallisation in presence of animal charcoal. Benzoic acid, which may still be present in the crude acid, is also easily removed, its barium salt being much less soluble than that of the meta-acid.

Barium metanitrobenzoate, $(C_7H_4(NO_2)O_2)_2Ba + 3H_2O$, crystallises from a hot concentrated solution in groups of small rhombic plates, but by spontaneous evaporation it is obtained in large, well-defined, rhombic plates of a honey-yellow colour. The *pure* metanitrobenzoic acid melts at 145°; from water it crystallises in short needles, but by spontaneous evaporation of an alcoholic solution, it is obtained in yellowish, large, well-defined prisms or rhombic plates. The acid and its salts are distinguished by their intensely sweet taste, whilst its

isomerides, in common with most nitro-compounds, taste intensely bitter. The yield of metanitrobenzoic acid is about 2 per cent. of the benzoic acid employed. C. S.

Atractylic Acid. By LEFRANC (Compt. rend., lxxvi, 438—440; also J. Pharm. Chim. [4], xvii, 187—193, and 263—267).

NEW researches on this acid, obtained by the author from the root of *Atractylis gummifera*, have shown that it may be regarded as the representative of a new class of acids formed by the union of compounds analogous to ethylsulphuric acid with those of which benzenesulphuric acid is an example.

Atractylic acid, when submitted to the action of ordinary saponifying agents (hydrates of calcium, potassium, &c.) behaves like the divalerosulphuric ether of a compound which the author has isolated and named *atractylin*. When heated with potassium hydrate above the melting-point of that substance, it is decomposed, with evolution of hydrogen, and formation of a solid resinous body of phenolic character, which is left as potassium salt, together with sulphate.

The saponification of atractylic or *atractylidivalero-sulphuric* acid may be effected in two stages. In the first stage valeric acid alone is disengaged, the acid thus modified preserving its type. The β-atractylic or *atractylidisulphuric* acid resulting from this action forms two series of salts, with two and three equivalents of metal:

$$\underset{\text{Neutral potassium atractylate.}}{C_{30}H_{51}K_3S_2O_{18}} + 2KHO = 2C_5H_9KO_2 + \underset{\text{Neutral potassium β-atractylate.}}{C_{10}H_{35}K_3S_2O_{16}}.$$

Atractylin is a gummy, inodorous substance, having a peculiar sweet, strong taste. It is very soluble in water and alcohol, but insoluble in ether. It has a slightly acid reaction, and combines with alkalis and alkaline earths, forming compounds soluble in water, but decomposed by boiling. Its solution in strong sulphuric acid is of a yellow colour, changing on warming to purple and violet. This reaction is characteristic of atractylates and β-atractylates.

Atractylin dissolves in nitric acid, without alteration in the cold, but is decomposed on warming. When boiled with very dilute acids, it undergoes decomposition and dehydration in a manner similar to salicin thus treated. It is resolved by the action of dilute solution of potassium hydrate into a crystalline substance (*atractyligenin*), and a peculiar sugar:

$$\underset{\text{Atractylic acid.}}{C_{30}H_{54}S_2O_{18}} = 2H_2SO_4 + 2C_5H_{10}O_2 + \underset{\text{Atractylin.}}{C_{20}H_{30}O_6}.$$

J. R.

Direct Formation of Aromatic Amido-derivatives. By H. SALKOWSKI (Deut. Chem. Ges. Ber., vi, 139—141).

THE production of dinitroaniline from dinitranisol takes place even at the temperature of boiling water. Tin and hydrochloric acid reduce

dinitraniline to triamidobenzene; the base itself is best obtained from its salts by distillation with quick-lime. As thus obtained, it is not pure, and melts at 340°, whilst the triamidobenzene from triamidobenzoic acid melts at 330°. Hofmann obtained only diamidobenzene by iron and acetic acid.

Picramide (trinitraniline) should give rise to tetramidobenzene. Oxidation, however, takes place and a base, $C_6H_2(NH_2)_2(OH)_2$ or $C_6H_2(NH_2)_2(O_2)$, is formed.

By the action of ammonia the two nitranisols give respectively Hofmann's metanitraniline and β-nitraniline; the former is produced only at 190°—200°, the latter at 140°, when aqueous ammonia of sp. gr. 0·93 is used.

Anisic acid, methyl-salicylic acid, and methoxybenzoic acid do not give the corresponding amido-acids by treatment with ammonia, but only the oxy-acids and phenol; bodies containing the group CO.OH, as well as the NO_2 groups, are more readily attacked than those containing only the latter.

C. R. A. W.

Amidomonochlorobenzenesulphonic Acid. By L. PRATESI (Gazzetta chimica italiana, ii, 555).

THE author has previously shown (*Gazzetta*, 1871, 685; *Chem. Soc. J.*, 1872, 245) that aniline phenylsulphonate subjected to dry distillation yields amidobenzenesulphonic acid (Gerhardt's sulphanilic acid), $C_6H_4\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right.$. To investigate the nature of this reaction he has also subjected to dry distillation, toluidine phenylsulphonate, aniline chlorophenylsulphonate, and monochloraniline phenylsulphonate. The first gave amidotoluenesulphonic acid or amidomethylbenzenesulphonic acid, $C_6H_3(CH_3)\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right.$, identical with that which Sell obtained by distilling a mixture of toluidine and fuming sulphuric acid; the second gave, no longer phenol, but monochlorophenol and amidobenzenesulphonic acid, identical with that which is obtained from phenylsulphonate of aniline; the third yielded, together with phenol, the new acid, *amidomonochlorobenzenesulphonic acid*, $C_6H_3Cl\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right.$. If, then, as Kekulé supposes, the above-mentioned constitution of amidobenzenesulphonic and amidotoluenesulphonic acid is correct, the reactions must take place in the manner represented by the following equations:—

$$\text{I.}\quad \underset{\text{Aniline phenylsulphonate.}}{C_6H_4\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right..C_6H_5NH_2} = \underset{\text{Phenol.}}{C_6H_4\left\{\begin{matrix}OH\\H\end{matrix}\right.} + \underset{\text{Amidobenzenesulphonic acid.}}{C_6H_4\left\{\begin{matrix}NH_2\\SO_3H.\end{matrix}\right.}$$

$$\text{II.}\quad \underset{\text{Toluidine phenylsulphonate.}}{C_6H_4\left\{\begin{matrix}OH\\SO_3H\end{matrix}\right..C_6H_4(CH_3)NH_2} = \underset{\text{Phenol.}}{C_6H_4\left\{\begin{matrix}OH\\H\end{matrix}\right.} + \underset{\text{Amidotoluenesulphonic acid.}}{C_6H_3(CH_3)\left\{\begin{matrix}OH\\SO_3H.\end{matrix}\right.}$$

$$\text{III. } C_6H_3Cl\left\{\begin{matrix}OH\\SO_3H.C_6H_5NH_2\end{matrix}\right. = C_6H_3Cl\left\{\begin{matrix}OH\\H\end{matrix}\right. + C_6H_4\left\{\begin{matrix}NH_2\\SO_3H\end{matrix}\right.$$

Aniline monochlorophenyl-sulphonate. Monochlorophenol. Amidobenzene-sulphonic acid.

$$\text{IV. } C_6H_4\left\{\begin{matrix}OH\\SO_3H.C_6H_4ClNH_2\end{matrix}\right. = C_6H_4\left\{\begin{matrix}OH\\H\end{matrix}\right. + C_6H_3Cl\left\{\begin{matrix}NH_2\\SO_3H.\end{matrix}\right.$$

Monochloraniline phenyl-sulphonate. Phenol. Amidomonochlorobenzenesulphonic acid.

That is to say, the phenylic radical which enters into the composition of amidobenzenesulphonic, amidotoluenesulphonic acid, &c., is the same as that of aniline, toluidine, &c.

In corroboration of this conclusion it may be added that Emile Kopp, having subjected to dry distillation the two isomeric phenylsulphonates of aniline derived from the two isomeric phenylsulphuric acids, obtained in both cases the same amidobenzenesulphonic acid; whereas if the phenylic radical of phenylsulphonic acid were the same as that which enters into the constitution of amidobenzenesulphonic acid, two isomeric amidobenzenesulphonic acids would probably have been obtained, the isomerism depending on the position of the radicals NH_2 and SO_3H with respect to the group C_6H_4.

H. W.

A New Red Colouring Matter from Aniline. By F. Hamel (Compt. rend., lxxvi, 376).

If sulphur chloride be added to 20—25 grams of aniline, with constant agitation, a red solid product is obtained almost immediately. On treatment with acetic acid and filtration, a red solution is produced, from which the colouring matter is deposited on evaporation as a black mass, soluble in acetic acid, alcohol, and ether. On addition of water to either of these solutions, a grey precipitate is thrown down.*

H. E. A.

On Griess' Phenylenediamine and Dibromobenzene. By T. Zincke and F. Sintenis (Deut. Chem. Ges. Ber. vi, 123—125).

The nitraniline obtained from the bromonitrobenzene melting at 38°, yields, on treatment with tin and hydrochloric acid, a phenylenediamine which is identical with that obtained by Griess. It sublimes in small, brilliant plates or ramified needles, and crystallises from ether or chloroform in well-defined, rectangular plates melting at 99°. We know therefore now the three nitranilines and phenylenediamines corresponding to the three brominitrobenzenes.

The nitration of solid dibromobenzene yields only one nitrobromobenzene melting at 84°. From this it appears probable that the bromine occupies the position 1 : 4, for a compound of this constitution

* The formation of a colouring matter in this way from aniline has already been noticed by Ad. Claus (*Zeitschr. f. Chem.* [2], vi, 691).—H. E. A.

can yield only one mononitro-product; the formation of two or more would certainly have proved that it is either 1:2 or 1:3 dibromobenzene.

C. S.

On Anthracenamine. By T. L. PHIPSON (Chem. News, xxvii, 97).

THIS new base may be obtained by adding anthracene in powder, in small quantities at a time, to ordinary nitric acid contained in a capsule which can be cooled if necessary. A soft reddish-brown mass is obtained which melts easily, and can be drawn out into long golden-yellow filaments. This product contains a certain quantity of mononitranthracene, $C_{14}H_9NO_2$, soluble in alcohol, from which it crystallises in small yellow needles. If the temperature is allowed to rise and the acid boils, several other products are obtained and much oxanthracene. The product is washed and placed in a flask with tin and hydrochloric acid, diluted with its own volume of water and boiled quietly for an hour, then filtered. The filtered liquid contains chloride of anthracenamine and tin chloride; the base is extracted by excess of potash which dissolves the tin oxide and leaves the anthracenamine. It is necessary to repeat the operation twice to get rid of all the tin.

Anthracenamine is a pale yellow powder, forming soluble and crystallizable salts with sulphuric and hydrochloric acids. It is very soluble in alcohol, but slightly soluble in water; its odour is very slight, and its taste is hot, pungent, and persistent, very like that of the unknown substance which exists in the Arum maculatum. Its acid salts produce with potassium bichromate a characteristic emerald-green colour, and finally precipitate a powder of this colour which is soluble in alcohol. This solution presents no marked peculiarity when viewed in the spectroscope. The reaction is as characteristic of anthracenamine as the blue colour produced in similar circumstances is of naphthylamine. It is not obtained, however, with lead peroxide or with calcium hypochlorite, but it is obtained with concentrated nitric acid.

Anthracenamine is easily decomposed; and from the percentage of nitrogen it contains, the author concludes that its composition may be represented by the formula, $C_{14}H_{11}N$.

J. B.

Hyoscyamine. By MERCK (N. Repert. Pharm., xxii, 117).

HYOSCYAMINE was described by Thorey as crystalline, but Höhn could only obtain it in an amorphous state. Merck finds that it forms a more or less coloured amorphous mass, which volatilizes on careful heating in hydrogen, and forms an oily distillate resembling conine in odour and appearance. It is easily soluble in alcohol and ether, and is readily taken up by this means from water; in benzene and chloroform it is only partially (?) soluble. By exposure to air it becomes yellow and brown and finally viscid, and possessed of an unpleasant smell; in this state it is only imperfectly soluble in ether.

It has a powerful alkaline reaction and completely neutralizes acids; the nitrate and oxalate are crystalline, the sulphate and hydrochloride amorphous.

Attempt to synthesize Tyrosin. By A. LADENBURG (Deut. Chem. Ges. Ber., vi, 129—131).

THE chemical behaviour of tyrosin is capable of explanation on the assumption that it is ethylene-oxyparaamidobenzoic acid (ethoxy-paraamidobenzoic acid ?), represented by the formula—

$$C_6H_4\left\{\begin{matrix}NH.OC_2H_5\\CO_2H.\end{matrix}\right.$$

The author has succeeded in preparing this body, by heating a mixture of equal molecules of ethylene oxide and paraamidobenzoic acid in sealed tubes at 50° for two days, and finds that it is only isomeric with tyrosin. It crystallises in prisms, difficultly soluble in cold water and alcohol, but easily soluble in hot dilute alcohol; it melts at 187° (paraamidobenzoic acid at 186°). Its aqueous solution is not precipitated by lead acetate, whereas even hot dilute solutions of para-amidobenzoic acid yield a highly characteristic crystalline precipitate of lead paraamidobenzoate and acetate, $C^7H^4NO^2.C^2H^3O^2.Pb$. It forms metallic salts, and also unites with acids. It is decomposed on heating, with evolution of carbonic anhydride, and a basic oil remains, yielding a crystalline sulphate, which, on analysis, gives numbers approximating to those required by the formula $(C_6H_7NC_2H_4O)_2H_2SO_4$. Possibly this compound may be obtained in greater quantity and purity by the action of ethylene oxide on aniline.

H. E. A.

Composition of the Volatile Oil of the Fruit of Pastinaca Sativa. By J. J. VAN RENESSE (Ann. Chem. Pharm., clxvi, 80—87).

THE oil prepared from the ripe fruit by distillation with water, was a colourless neutral liquid, having a not unpleasant smell and aromatic taste. With potassium bisulphite it gave no indications of forming a crystalline compound. Sp. gr. at 17·5° = ·8672.

By fractional distillation, the greater part was separated with a boiling point between 244° and 245°. Submitted to analysis, it gave numbers corresponding to the formula $C_6H_{12}O$, but when treated with alcoholic potash it furnished octylic alcohol, identical with that described by Zincke, and butyric acid, which, by its high boiling point, and by the character of its calcium salt was recognised as the normal acid.

The lower and higher fractions of the original parsnep oil were too small in amount to admit of purification by redistillation. They were, however, found to be compound ethers derived from an octyl alcohol, and furnished two acids which seemed to be propionic and butyric.

The author appends a preliminary notice of the amines derived from the octyl alcohol.

With regard to octylamine, he has observed that it unites readily with water to form a crystalline compound.

W. A. T.

On Picrotoxin. By H. Böhnke-Reich (Arch. Pharm. [3], i, 498—505).

This research, made twelve years ago, and now first published, does not appear to add anything to the existing knowledge of picrotoxin.

J. R.

On Flavin. By A. Ott (Chem. News, xxvii, 98).

This paper consists principally of a summary of the results published by Bolley, Leeshing, and Schlumberger on flavin and on processes for producing dyes from quercitron.

J. B.

Physiological Chemistry.

Experimental Researches on the Influence of Changes in Barometric Pressure on the Phenomena of Life. By Paul Bert (Compt. rend., lxxvi, 443—446).

In former papers (see this Journal, vol. xxvi, pp. 831 and 1029), the author mentioned the poisonous action of oxygen or compressed air. In his present paper, he states that in dogs convulsions begin when the external pressure of oxygen is about $3\frac{1}{2}$ atmospheres, or 17 atmospheres of air, and death occurs at 5 atmospheres of oxygen. From an examination of the blood, he finds that oxygen acts as a rapid poison when the quantity present in arterial blood rises to 35 per cent. This is not quite double the normal amount. Poisoning by oxygen is characterised by the presence of convulsions, which, according to their intensity resemble various forms of tetanus, epilepsy, or poisoning by strychnine or phenol. They are due to an exaggeration of the excito-motor power of the spinal cord, and are temporarily arrested by chloroform. They are accompanied by a considerable and constant diminution in the internal temperature of the animal.

T. L. B.

Researches on the Oxidising Power of Blood. By P. Schützenberger and Ch. Risler (Compt. rend., lxxvi, 440—442).

The authors are able to detect $\frac{1}{100}$ c.c. of oxygen dissolved in water, and to determine the amount of oxygen contained in blood, by adding to a measured quantity of it an amount of standard solution of sodium sulphite sufficient to absorb all the available oxygen at once, and leave an excess (see this Journal, 1873, p. 88). The amount of excess is estimated by means of a solution of indigo-carmine. The titration is conducted in an atmosphere of hydrogen, and kaolin is added to the liquid in order to render the changes in tint more perceptible. The quantity of oxygen can be determined within 2 per cent.

This estimated amount is less than the real one, and the error is due

to the colour of the blood obscuring the reaction. The authors find that the oxygen of the blood does not act on the sulphite like free oxygen, but like oxygen combined with ammoniacal cupric oxide. Fresh ox blood, saturated with oxygen, possesses, in respect of the sulphite, an oxidising power equal to 45 per cent. of oxygen. Blood deoxidised by the air-pump, or by carbonic oxide, has an oxidising power of 25 or 26 per cent. The oxygen removed by the air-pump is thus only 19 per cent., and blood saturated with oxygen has, therefore, an oxidising power 1½ times greater than has been hitherto attributed to it by calculations made on the amount of oxygen extracted from it by the air-pump or by carbonic oxide. This excess of oxygen exists in a more stable combination, and can only be removed by reducing agents. A 10 per cent. solution of blood, saturated with oxygen, and then treated with an excess of sulphite, gives the spectrum of reduced hæmoglobin and assumes a reddish-violet colour. On again estimating the oxygen after agitation with air, it furnished the same quantity as at first.

T. L. B.

On Tissue Change in the Animal Body after Blood-letting.

By Jos. Bauer (Zeitsch. f. Biologie, viii, 567—603).

The author's experiments upon dogs consisted of two series. The first was for the purpose of determining the amount of albumin decomposed daily, and the second, to estimate the decomposition of fat in the organism before and after blood-letting.

The decomposition of albumin was estimated from the urea excreted by dogs whose excretion of urea was kept constant by careful dieting, or which were entirely deprived both of food and water. In all cases the metamorphosis of albumin was increased by blood-letting.

In one dog, weighing 20 kilograms, whose excretion was kept constant, the daily amount of urea was 35.5 grams, or 16.6 grams of nitrogen. Four hundred cub. cent. of blood were then drawn from the crural vein. During the three following days the daily excretion of urea was about 7 grams above the average, and in the three days amounted to 21·7 grams of urea or 10.2 of nitrogen. On the fourth day it became nearly the same as before the operation. The urinary water increased together with the urea after blood-letting, but the specific gravity of the urine was higher than before.

As the excess of nitrogen passed was not contained in the food, it must have been derived from the body, and in the four days succeeding the phlebotomy, it corresponded to 65 grams of dry albumin or 298 grams of muscle decomposed in the organism. A dog of the same size as the first was deprived of food, and on the seventh day of fasting 256 c.c. of blood were drawn, and on the tenth day 400 c.c. more. After the first blood-letting the excretion of urea, which had been steadily falling, rose 5·06 grams or 78 per cent., and after the second it rose 3·36 grams or 37 per cent. Assuming that the daily excretion, if blood had not been drawn, would have been 7·5 grams, an estimate rather too high than too low, the total increase of urea caused by the extraction of blood would be 19·8 grams or 9·2 of nitrogen, correspond-

ing to 271 grams of muscle. The total increase of nitrogen is less when the animal is starved then when it is supplied with food, as in the former case it only amounted to 9·2 grams of nitrogen in seven days after blood had been twice drawn, while in the latter it was 10·2 grams in three days after one blood-letting. The percentage increase of urea is, however, greater during fasting. The quantity of urine was increased, along with the solids, although the dog got no water. The specific gravity increased at the same time. After the second blood-letting the dog drank 630 c.c. of water, but the urine was only increased by about 20 c.c., and therefore the greater part of the water was probably retained in the body. The author has also observed an increase in the excretion of urea after blood-letting in the case of a man suffering from croupous pneumonia.

The experiments on the decomposition of fat were made on a small dog weighing 4½ kilograms, placed in a small respiration apparatus made after Pettenkofer and Voit's model. When blood was drawn during a period of fasting, the excretion of carbonic acid was not altered at first, but the consumption of oxygen and excretion of water were diminished. After fasting for 20 hours more, however, the excretion of carbonic anhydride, as well as that of water, and the consumption of oxygen, became much less. A greater proportion of the oxygen consumed was excreted as CO_2 after the blood-letting than before. When the blood was drawn shortly after a meal, the excretion of carbonic anhydride and water, and the consumption of oxygen were all increased, especially the two latter. The next day, however, they were all diminished. The proportion of oxygen consumed to the carbonic acid excreted, became less immediately after the blood-letting, but it afterwards rose above the normal amount. The author details several experiments of Voit and Rauber, which confirm his own results. As the excretion of carbonic anhydride is diminished after blood-letting although the decomposition of albumin is increased, it is evident that the combustion of fat in the organism must be less. At first the combustion is only lessened in comparison with the increased metamorphosis of albumin, but afterwards it becomes absolutely diminished. In consequence of this, an accumulation of fat not unfrequently takes place in the body after blood-letting. The author explains the increased transformation of albumin after blood-letting by the supposition that, on account of the diminution in the amount of circulating albumin, more organ-albumin is converted into circulating albumin in consequence of the loss of blood (see this Journal, 1873, p. 285). He lays great stress on the difference between the explanations of O. Weber and of Voit. The former supposes that combustion takes place in the *blood* contained within the vessels, while Voit supposes that it takes place wherever living *cells* are present either in the blood or tissues. The author also discusses the effects of blood-letting in disease, but for this we must refer to the original.

T. L. B.

Determination of the Absolute Mass of the Blood. By J. Steinberg (Pflüger's Archiv., vii, 101—187).

A modification of Preyer's method for the determination of the mass of the blood in an animal is recommended by the author. The operation is performed as follows.

Equal quantities of blood are placed in two hæmatinometers; water is then poured into the one, and into the other a solution obtained by washing out the vessels of the animal with a solution of sodium chloride, and infusing the tissues. The addition is continued until the liquids in the two hæmatinometers exhibit an equal intensity of coloration; and this is determined by finding the point at which light begins to appear in the green of the spectrum. As the wash-water already contains a small quantity of blood, it is obvious that more of the wash-water will be required to be added to the blood in the one hæmatinometer than of water to the other, in order to arrive at the same state of concentration. We have now all the data necessary for the determination of the quantity of blood in the animal.

Let y be the required mass of the blood;

- m, the weight of blood employed at the beginning of the experiment;
- b, the quantity of blood placed in each hæmatinometer;
- a, the quantity of water added to the one hæmatinometer;
- c, the quantity of wash-water required to be added to the other hæmatinometer;
- d, the total volume of wash-water;
- x, the unknown quantity of blood contained in c.

Then—

$$x = \frac{b(c - a)}{a + b}, \text{ and}$$

$$y = m + \frac{d}{c} \cdot \frac{b(c - a)}{a + b}.$$

Full details are given as to the mode of performing the experiments. The following are the relative weights of the blood and of the bodies of the animals obtained by this method:—

Rabbits......	1 : 12·3—13·3
Guinea-pigs..	1 : 12·0—12·3
Dogs........	1 : 11·2—12·5
Puppies	1 : 16·2—17·8
Cats........	1 : 10·4—11·9
„ (fasting)	1 : 17·8
Kittens......	1 : 17·3—18·4

T. S.

Quantitative Determination of the Carbon Oxide combined with Hæmoglobin: Elimination of Carbon Oxide. By N. Gréhaut (Compt. rend., lxxvi, 233—236).

The carbon monoxide is determined by comparing the relative proportions of oxygen capable of being absorbed by normal blood, and by

the blood containing the carbon monoxide respectively; the carbon oxide prevents the absorption of a volume of oxygen equal to its own.

The author finds that in animals suffering from carbon oxide intoxication, that gas is eliminated unchanged, and not as carbon dioxide: hence artificial respiration is recommended to prevent a fatal issue in cases of poisoning by the former gas.

T. S.

Influence of Crystalline and Amorphous Quinine on the White Blood-corpuscles, and on the Formation of Pus. By G. KERNER (Pflüger's Archiv., vii, 122—138).

A PHYSIOLOGICAL memoir forming an experimental criticism on the researches of Geltowski, Binz, Stricker, and others, on the action of quinine on the white blood-corpuscles.

T. S.

Chemistry of Vegetable Physiology and Agriculture.

The Light Emitted by Leaves. By VOGEL (Berichte der K. b. Akad. d. Wissenschaften, 1872, 133—137).

GREEN leaves always appear black in photographs. Roscoe showed that with variegated mint the light from the green portion of the leaf had no photographic effect. The author has experimented with variegated leaves, and finds that in some cases the portion not green equally fails of photographic effect. In the case of a leaf green on the upper side, but red on the under, when the green side was exposed to light, and the red side towards the plate, no silver was reduced; but on reversing the leaf, reduction took place. As the rays which reduce silver salts are not consumed by plants for the decomposition of carbonic acid, the cause of their retention requires elucidation.

R. W.

Is Peat Smoke Injurious to Vegetation? By Prof. PRESTEL (Ann. der Landwirthschaft, 1872, 750).

STATISTICS of the rye harvests and of the number of days on which peat smoke was prevalent in Westphalia during the years 1862 to 1871, show, contrary to the popular opinion, that in the years during which the air was most impregnated with smoke, the harvest was above the average, and that in the years during which peat-burning was unusually small, the rye harvest was below the average.

E. K.

Influence of Coal Gas on the Growth of Trees. (Ann. der Landwirthschaft, 1872, 764.)

IN the botanical garden of Berlin, a maple and a lime tree, $3\frac{1}{2}$ to $5\frac{1}{2}$ feet in diameter, were treated daily, from July, 1870, for six months, with

100 cubic feet of gas, introduced $2\frac{1}{2}$ feet under the surface of the soil, and about 3 or 4 feet from the trees; they began to look sickly after a month's exposure to the action of the gas, the maple died in the following spring, and the lime in the summer. An examination of the roots showed that the poisoning begins at the growing ends of the roots, and that the bark of the roots is not acted on. In another experiment, 25 cubic feet of gas were daily passed into a plot of ground having a surface of 144 square feet, and on which twelve young trees had been growing for one and a-half years; the trees showed signs of poisoning in a week's time, where the surface of the soil had been firmly stamped down, and in a month all the trees had lost their leaves.

E. K.

Influence of Metallic Salts on the Vegetation of Aspergillus Niger. (Ann. der Landwirthschaft, 1873, 93.)

In "Etudes chimiques sur la végétation," Jules Raulin gives the results of some experiments on the action of salts on the growth of fungi. The following is the composition of the solution most favourable to the growth of aspergillus: water, 1,500 grams; sugar, 70; tartaric acid, 4; ammonium nitrate, 4; ammonium phosphate, 0·6; potassium carbonate, 0·6; magnesium carbonate, 0·4; ammonium sulphate, 0·25; zinc sulphate, 0·07; ferric sulphate, 0·07; potassium silicate, 0·07. The action of zinc salts is remarkable: the presence of $\frac{1}{50,000}$ of zinc sulphate in the solution produces a crop three or four times as great as in the absence of zinc. Want of iron salts is little detrimental to the growth of the mould, but the addition of $\frac{1}{100,000}$ of silver nitrate, or $\frac{1}{500,000}$ of mercuric chloride to the solution is sufficient to prevent any further development.

E. K.

Digestibility of the Fat of Hay. By J. König (Landw. Versuchs-stationen, xvi, 40—47).

The author replies to the objections of E. Schulze (*Jour. Chem. Soc.*, [2], x, 1037), to his former statements. König now admits that the fat of hay does not contain glycerides. He denies, however, that his method of separating the fats by their solubility in cold alcohol is incapable of throwing light on the quantity of digestible fat present. The evidence shows that, on the whole, the low-carbon fats are digested, while the high-carbon fats are not digested; and among the hay fats those containing less carbon are those most soluble in cold alcohol, though some of the higher carbon fats are also soluble. More extended researches are promised.

R. W.

Nature of the Fats in Meadow Hay. By J. König and J. Kiesow (Landw. Versuchs-stationen, xvi, 47—56).

The present paper is preliminary only. The purified ethereal extract was separated into a fluid fat soluble in cold alcohol, and a solid waxy

matter sparingly soluble in cold alcohol. Treated with alcoholic potash, the greater part of both these fats saponified. The soaps obtained were separated into parts of different solubility, then decomposed, and the fatty acids examined. The acids appear to be cerotic acid, and various members of the acrylic series not yet identified.

The unsaponified portion of the waxy matter contains ceryl alcohol and a hydrocarbon which melts at 73° and yields to analysis C 84·42 and H 15·13. In a previous paper (*Journ. Chem. Soc.* [2], ix, 1194), König had shown that the waxy matter separated by cold alcohol from the fat of oat straw and pea straw, contained more carbon than the highest known member of the fatty series. Other ingredients of the unsaponified residues are not yet identified.

R. W.

Composition and Feeding Value of Clover at different stages of Growth. By E. Heiden (Ann. der Landwirthschaft, 1873, 85, from Amtsblatt für die landwirthschaftlichen Vereine im Königreich Sachsen, 1873).

The author concludes from his experiments that clover should be cut at the commencement of flowering, as there is no essential increase in the crop after this time, and a falling off in the feeding value, from decrease in albuminoïds and increase in fibre, as the clover grows older.

E. K.

Feeding Experiments with Sophisticated (denaturirten) Cattle Salts. By E. Heiden (Ann. der Landwirthschaft, 1872, 876).

Experiments with oxen and calves, showed that cattle will voluntarily consume salt containing 10 per cent. of ferric oxide, and 10 per cent. of wormwood, and that it is without any injurious influence on them. Salt containing 10 per cent. of gypsum, or 20 per cent. of magnesium chloride, is also readily consumed by cattle.

E. K.

The Bitter Apple as an Article of Food. By F. A. Flückiger (N. Report. Pharm., xxi, 46—59).

The bitter apple, bitter cucumber, bitter gourd, or colocynth (*Citrullus Colocynthis* Schrader), is a creeping cucurbitaceous plant which grows abundantly in the Sahara in Arabia, and on the Coromandel Coast, and is found in some of the islands of the Ægean Sea. The fruit, which is about as large as an orange, contains an extremely bitter and drastic pulp, from which colocynth is obtained. This pulp is said to be eaten by buffaloes and ostriches, but is quite unfit for human food. The seed-kernels, however, which contain but a very small quantity of bitter principle, are used as food by some of the natives of the African desert. For this purpose the seeds are first freed from pulp by roasting and boiling, and subsequent treading in sacks, and then deprived of

their coatings—which are also decidedly bitter—by grinding and winnowing. A single kernel thus separated, has only a mild oily taste, but several, if tasted together, exhibit a distinct bitterness. The average weight of a seed is about 45 milligrams, of which the kernel constitutes only one-half. The kernels contain about 48 p.c of a fatty oil, and 18 p c. of albuminous substances, besides a small quantity of sugar, and may, therefore, be regarded as a sufficiently nutritive esculent. The inorganic constituents of the seeds amount to 2·48—2·7 per cent.; the pulp of the fruit contains a much larger proportion, viz, 11 p.c.

H. W.

Analysis of Agaricus Fœtens. By M. Sace (Compt. rend., lxxvi, 505).

Water	67 20
Mannite	0·60
Pectic acid	0 09
Fibrin	4·66
Bassorin	1·55
Ligneous matter	20·09
Fat, acids, colouring and odorous matter	0 68
Ash	5·13
	100·00

C. R. A. W.

On the Constituents of the Seed of the Yellow Lupine. By Hermann Ludwig (Arch. Pharm. [3], i, 494—498).

A summary of previous researches, containing nothing new.

J. R.

On Alcoholic Fermentation by means of Mucor Mucedo. By A. Fitz (Deut. Chem. Ges. Ber., vi, 48—58).

De Bary, in 1857, and afterwards Rees discovered that the mould-fungus, *mucor mucedo*, immersed in saccharine solutions, is capable of setting up the alcoholic fermentation, the spores of the fungus multiplying by gemmation after the manner of beer-yeast. The mucor cells, however, are easily distinguished from yeast cells by their enormous size and by the red coloration produced by zinc chloride in their cellulose envelope. In the presence of air, mucor also develops a luxuriant mycelium; beer-yeast produces no mycelium, but, under suitable conditions, generates ascospores.

The author has made a number of experiments upon the alcoholic fermentation induced by mucor. He finds that the spores of this fungus develop differently according to the presence or absence of oxygen. In the absence of oxygen, they multiply by gemmation, and alcoholic fermentation is set up, but in the presence of air, a luxuriant reticulated mass is produced, no fermentation occurring at first, but only oxidation of the sugar through the agency of the mycelium. This

continues till the oxygen is consumed, when the mycelium breaks up into isolated cells, and fermentation commences.

Mucor fermentation proceeds best at a temperature between 25° and 28°. The gas evolved is pure carbonic anhydride.

Mucor yeast is very sensitive to the presence of alcohol, and the fermentation soon comes to an end. From the author's experiments it appears that, practically, mucor can only be employed for the fermentation of solutions containing less than 7 per cent. of sugar.

Succinic acid is formed in the mucor fermentation, but the author has not been successful in detecting glycerin in the product of the reaction.

Dextrin, inulin, and milk-sugar do not ferment under the influence of mucor.

W. A. T.

Analytical Chemistry.

Technical Gas Analyses. By C. Winkler (J. pr. Chem. [2], vi, 301—333).

The apparatus used by the author is a modified form of Hofmann's apparatus for decomposition of ammonia, &c. It consists of a two-limbed tube, one limb of which is wider than the other and furnished near the upper and lower ends with glass stopcocks; the space between these being graduated into fifths of cubic centimeters.

The second limb of the tube is connected with the first by means of caoutchouc tubing; it is also furnished with a stopcock (as in Hofmann's apparatus). The apparatus may be turned upon its stand either vertically or horizontally, as required. The gas to be analysed is made to pass through the apparatus for some time, the stopcocks are then closed, and the volume of gas in the graduated tube is noted. The liquid which is to act as absorber is poured into the second tube, and by opening the lower stopcock of the graduated tube, some of it is made to pass into this latter. (Special peculiarities in the stopcock separating the two tubes by which any air-bubbles are allowed to escape, are described and figured in the original paper.)

To promote absorption, the apparatus is placed horizontally for a few minutes. After a little time the vertical position is resumed, and more liquid allowed to enter, and so on, until on opening the connecting stopcock no further in-rush of liquid takes place. The level of the liquids in both tubes being made to coincide, the volume of liquid in the graduated tube corresponds with the volume of gas absorbed. If several constituents of a gas are to be estimated, a number of these instruments is necessary.

To reduce the gas to a stated temperature, generally that of the absorbing liquid, it is made to pass through a small flask containing mercury, which is surrounded by a quantity of the liquid at the ordinary temperature of the air. Generally the gases are passed through wetted cotton-wool before entering the graduated tube.

The author then discusses the various liquids used for absorbing

different gases, and gives numbers expressing results obtained by him.

Water vapour is absorbed by strong sulphuric acid, carbon dioxide by caustic potash, and so on. A mixture of oxygen, carbon dioxide, sulphur dioxide, and nitrogen is analysed by absorbing the first three gases with pyrogallic acid in caustic potash; in another trial the oxygen and carbon dioxide are absorbed by caustic potash alone; and in a third, the sulphur dioxide only is removed by a solution of iodine in potassium iodide.

Carbon monoxide is absorbed by a solution of cuprous chloride in hydrochloric acid; if the gas contains at the same time carbon dioxide and oxygen, these are removed by bubbling it through tubes containing a solution of pyrogallic acid in caustic potash previous to its entering the apparatus.

The numbers given are generally within 0·1—0·3 per cent. of the theoretical amounts.

M. M. P. M.

Detection of Traces of Manganese. By R. Böttger (Zeitschr. Anal. Chem., xi, 433).

A very small quantity of the substance to be examined (organic or inorganic) is thrown into a few grams of potassium chlorate melted in a test-tube. Manganese, if present, is indicated by the appearance of a reddish colour after the salt has completely cooled. The author has in this way detected manganese in a piece of wood-charcoal scarcely large enough for weighing, and in a red human hair.

H. W.

Analysis of Galena. By G. C. Wittstein (Zeitschr. Anal. Chem., xi, 460).

Storer (*ibid.*, ix, 514) proposed to assay galena by decomposing it in the finely pulverised state with hydrochloric acid and metallic zinc. Wittstein, however, finds that the decomposition is far from being complete, from $\frac{1}{4}$ to $\frac{1}{3}$ of the galena remaining unacted upon, even when a large excess of zinc is used.

H. W.

Method of Estimating Asparagin. By R. Sachsse (J. pr. Chem. [2], vi, 118—127).

The method depends on the facts that asparagin is converted by prolonged heating with hydrochloric acid solution into ammonia and aspartic acid, and that the latter and aspargin are both unaffected by brominated soda solution, so that by determining by Knop's method (*Zeitschr. f. Analyt. Chem.*, ix, 225) the amount of nitrogen liberated on shaking an asparagin solution, after it has been digested with hydrochloric acid, with the brominated soda-solution, the necessary data are obtained for the calculation of the amount of asparagin present.

A number of verification experiments with weighed quantities of

asparagin (·03—·3 grm.) dissolved in 100 c.c. of water, and heated for 12 hours with 10 c.c. of ordinary hydrochloric acid, also with weighed quantities of asparagin mixed with 10 grams of fine pea-flour (which contains no asparagin) are quoted, and show that the method is capable of yielding highly satisfactory results.

Although an aqueous solution of asparagin may be preserved unchanged, an impure solution containing albuminous substances cannot; it is therefore necessary to extract it from the vegetable substance in which the amount of asparagin is to be determined as rapidly as possible. The method which the author adopted in the extraction of the asparagin from the mixture with pea-flour, and which he recommends for general use is as follows: the 10 grams of flour were heated for 15 minutes with 200 c.c. of a mixture of equal volumes of ordinary alcohol and water in a flask connected with a reversed condenser; the source of heat was then removed; and 5 c.c. of a cold saturated solution of mercuric chloride diluted with an equal volume of water added to the hot solution, the whole well shaken, and filtered through a moderately large fluted filter. The precipitate, which was brought as completely as possible into the filter, was then washed with a second 200 c.c. of heated alcohol and water mixture, afterwards three or four times with cold water. The entire filtrate thus obtained (500—550 c.c.) was evaporated on the water-bath; the residue dissolved as completely as possible in the least possible quantity of water, and the solution and the undissolved matter were introduced into a small beaker, and saturated with sulphuretted hydrogen. The precipitate of mercuric sulphide was then removed by filtration and washed with hot water, and the filtrate (100—120 c.c.) was mixed with 10 c.c. of hydrochloric acid and heated to boiling for an hour in a flask attached to a condenser; after cooling, the ammonia was determined by Knop's method. The author shows that the amount of decomposition which asparagin suffers previous to the treatment with hydrochloric acid, is almost inappreciable. Heating for 1—1·25 hours with the acid was found sufficient to convert the whole of the asparagin into aspartic acid and ammonia; longer heating gave too high results. It is proposed to employ this method in investigating the formation and movement (*Wanderung*) of asparagin which occurs during the germination of the Leguminosæ.

H. E. A.

On Hager's Method of Estimating Cinchona Alkaloïds.

By O. Medin (Zeitschr. Anal. Chem., xi, 447).

This method, published by Hager in 1859 (*Zeitschr.*, viii, 477) consists in digesting 10 grams of cinchona bark for a short time with about 130 grams of water and 20 drops of potash-ley, sp. gr. 1·35; then adding 15 grams of sulphuric acid, sp. gr. 1·115; boiling for 20 minutes; adding water after cooling, so as to make up the liquid to 110 c.c.; filtering; and precipitating the measured filtrate with 50 c.c. of picric acid solution saturated in the cold. The molecular weight of cinchonine being but little less than that of quinine and quinidine, the quantity of alkaloïds present may be calculated with sufficient accuracy

from the weight of the precipitate obtained from 100 c.c. of the filtrate.

Objections have, however, been made to this method by van der Burg (*ibid*, ix, 305), first because the extraction of the alkaloids is incomplete; secondly. because the precipitate is not of constant composition, foreign matters being carried down together with the alkaloids. Medin, however, finds, as the result of a large number of experiments, that the method is perfectly trustworthy, the extraction of the alkaloids being complete, their precipitation by picric acid also complete, and the slight error arising from the simultaneous precipitation of other substances being compensated by a slight loss of the precipitated picrate during washing. Moreover, the method is easy and expeditious.

H. W.

Detection of Curarine. By F. A. Flückiger (N. Repert. Pharm., xxii, 65).

Curarine yields with sulphuric acid and potassium dichromate a blue-violet tint not unlike that produced by strychnine under the same circumstances, but more permanent; the brown colouring matters apt to be present in crude curarine interfere much with the reaction; neither precipitation by lead acetate nor treatment with animal charcoal is sufficient to purify an alkaloid thus contaminated.

Curarine extract (best prepared by means of glycerin) yields an amorphous precipitate of curarine chromate with potassium-dichromate (neutral chromate does not answer so well): this precipitate is more soluble in water than the corresponding strychnine compound which, moreover, is crystalline; when air-dry, it dissolves in sulphuric acid with a pure and intense blue colour, whereas the strychnine salt gives a violet tint; in neither case could the colouring matter be separated and examined by itself. Phosphoric acid cannot be substituted for sulphuric acid in this reaction.

Potassio-mercuric iodide and potassium platinocyanide precipitate curarine from its glycerin solution, as amorphous flakes, which do not become crystalline when dissolved in alcohol, and separated from this solution; the corresponding strychnine compounds readily become crystalline by this treatment.

Curarine may be separated from strychnine by means of benzene, in which the former is insoluble; it is readily soluble in water.

C. R. A. W.

The Recognition of Colours on Textile Fabrics. By L. Gabba (Gazzetta chimica italiana, ii, 381—385).

The author remarks, that although dyers can occasionally guess the nature of the colouring matter employed in dyeing a fabric, yet they are very likely to err, so that it would be much better to have a methodical process for determining the nature of the colouring matters, similar to that employed in inorganic analysis. In the present paper the results of the examination of the following blue dyes are

given:—Indigo, Saxony blue, Prussian blue, logwood blue, aniline blue (insoluble and soluble), *bleu faïence* (a variety of indigo blue), mixture of indigo and logwood blue, of Saxony and Prussian blue, of indigo and Prussian blue, azuline, ultramarine, and molybdenum blue. The reactions of the first five have been already accurately described by Stein (*Zeits. Analyt. Chem.*, 1870, and *Dingler's Polytech. Jour.*, 1869), but insoluble aniline blue is changed by soda to a brownish red, whilst the soluble blue becomes colourless; azuline under similar circumstances changes to violet. In mixed vat and logwood blues, acids (other than nitric acid) destroy the latter and leave the former unchanged. When mixtures of Saxony and Prussian blue are treated with hypochlorites, the former is destroyed and the latter left. A mixture of indigo and Prussian blue acquires a greenish shade when treated with soda, owing to the Prussian blue changing to yellow. Molybdenum blue is recognised by the ash of the fabric containing molybdic acid and tin, whilst ultramarine becomes colourless and evolves sulphuretted hydrogen when treated with an acid.

C. E. G.

Estimation of the Extract-contents of Beer and —. By OSCAR KNAB (Dingl. polyt. J., ccvi, 485—489).

POINTS out again the obvious fact that the specific gravity of a solution containing various bodies of different specific gravities, in variable proportions, cannot be a measure of the absolute weight of those solids contained in the solution.

C. H. G.

Adulteration of Wax with Tallow. By HARDY (Chem. Contr., 1872, 538).

WAX floats in alcohol of 29°. By observing the strength of the alcohol in which the sample floats, the percentage of wax may be deduced.

If the alcoholometer shows		29·°	the wax contains	100	per cent. wax.
"	"	39°·63	" "	75	"
"	"	50°·25	" "	50	"
"	"	60°·87	" "	25	"
"	"	71°·50	" "	0	"

M. M. P. M.

Detection of Fusel Oil in Spirits of Wine. (N. Repert. Pharm. xxii, 118.)

BOUVIER places a few fragments of potassium iodide in a test-tube, adds the spirit, and gently shakes the liquid; the formation of a yellow coloration indicates the presence of fusil oil. Boettger finds that this coloration is due, not to amylic alcohol, but to the action of acids (acetic, valerianic, &c.) on the iodide.

Potassium permanganate solution is much more readily decolorised by amylic than by ethylic alcohol.

C. R. A. W.

Technical Chemistry.

Various Uses for Blast-furnace Slags. By T. Egleston (Dingl. polyt. J., ccvi, 457—462).

The brittleness of these slags is the chief objection to their use as a road-mending material. When they are devitrified by leaving them to cool slowly, in large masses and under considerable pressure, they furnish an excellent road material; about half the mass of slag is thus completely devitrified.

The following are outlines of processes described for the preparation of building stones:—The slag is run from the blast-furnace into a semicircular vessel on moving wheels and having its bottom covered three centimeters deep with sand and coke-dust. By means of a bent iron implement, the slag is mixed with sand and coke-dust till the escape of gases has nearly ceased and the mass is sufficiently tough. With the same tool it is next pressed into a mould furnished with a [illegible] which is forced down as soon as the escape of gas ceases. The red-ho[illegible] is then placed in the cooling-oven, covered with coke-dust, and allowed to remain three or four days to cool completely. These stones are impervious to damp and make good foundations. According to another method, the slag, which should contain from 38 to 44 per cent. of silica, is run down a shoot into a large cavity, and there covered over with sand and ashes, and left to cool for five to ten days, when it is distributed in moulds and there hardens. In certain parts of Belgium slag is poured upon iron plates and cooled by water, and thus a kind of glass is manufactured.

In other districts the slag is granulated as it flows from the blast-furnace by means of a stream of water. The granulated slag is preferred by the puddlers to sand, for the moulds for pig-iron. The slag-gravel may be advantageously substituted for sand in mortar making, a more rapid hardening being thus secured, a matter of great moment in building foundation-walls.

Artificial stone is also manufactured from this granulated slag and used for building purposes, furnishing warm, dry houses, of handsome appearance.

When stones for building with enamelled surfaces are required they are obtained, in some parts of Europe, as follows:—The unburnt bricks are covered with granulated slag, and after drying, are burnt in a furnace where they do not come in contact with carbon. The stones are completely glazed, and, according to the different kinds of slag used, are tinted of different colours. This operation is also employed advantageously with tiles, pipes, and earthenware.

If in the preparation of fire-proof bricks a certain proportion of a mixture of clay and granulated slag be added to the mixture, very hard and durable fire-bricks are obtained. These have been tested in a brass furnace, and experiments are being tried as to their applicability to building puddling furnaces. This granulated slag may also be advantageously used for manure. Blast-furnace slag has also been drawn out in fine threads or filaments, furnishing the so-called

"furnace-wool." This substance being a very bad heat-conductor, has suggested various household and other uses. A cheap and valuable cement, said to be equal to Portland cement, has been prepared from the finely-granulated slag, which will also resist well the action of acids.

W. S.

To produce Opacity in Glass. By P. WEISKOPF (Dingl. polyt. J., ccvi, 468).

FLUOR spar, rubbed to a fine powder, is mixed with concentrated sulphuric acid to a thin paste, and applied with a lead instrument to those parts of the glass which it is desired to frost or make opaque. Fine frosted designs may thus be produced on smooth transparent glass. The article should, after the above treatment, be gently heated in an iron vessel, with cover and funnel passing to a chimney; after cooling, it is finally washed with dilute alkali, and rubbed over by a brush with clean water.

W. S.

Basic Ferric Chromate. By B. KLETZINSKY (Dingl. polyt. J., ccvii, 83).

THIS substance forms a fine yellow, being especially useful when applied with soluble glass, with which it forms a hard cement. With ultramarine it gives a beautiful green colour. It is prepared by continued boiling of a solution of 433 parts by weight of crystallised ferric chloride with 1473 parts of potassium permanganate.

M. M. P. M.

The Purple of the Ancients and the Colouring Matter found in the Sarcophagus of St. Ambrose at Milan. By G. BIZIO (Gazzetta chimica italiana, ii, 433—443).

THE author, referring to a recent paper on the same subject (*Gaz. chim. ital.*, 1870, p. 78, and this Journal, xxv, 1103), points out that it is almost impossible that the blue colour found in the sarcophagus could be indigo, as that dye was not introduced into Europe before the middle of the sixteenth century, whereas the murex purple was certainly in use in the time of Charlemagne. He then gives a parallel, consisting of a series of reactions of indigo and the murex purple, showing that it is possible that the colouring matter examined by Frapolli, Lepetit, and Padulli may be Tyrian purple, especially if the latter had been made wholly or partly from the *Murex trunculus*, since this contains, besides the purple, a red colouring matter.

C. E. G.

Nature of the Black Spots produced in Dyeing with Cochineal. By G. GUIGNET (Chem. Centr., 1873, 71).

THESE spots have been found to arise from the presence of iron, especially in the tin-preparations used as mordants in red dyeing with cochineal; when tin-salts free from iron are used, they never occur.

H. W.

Red Coloration of White Lead. By J LORSCHEID (Deut Chem Ges Ber, vi, 21—22) —The white lead examined by the author was obtained by the South-German process Lead-plates are hung up in a vaulted chamber in which vapours of acetic acid and carbon dioxide are passed Sometimes the product contained layers of a red substance, and on examining the conditions under which this was formed, it was found that the cause was a deficiency of carbon dioxide, the connection between the coke-stove and the conducting pipe being so imperfect that vapour of acetic acid escaped through the latter As soon as this defect was remedied, a good white lead was obtained, and by bringing the red-coloured plates again in the chamber, the colour was removed The red substance consists of oxides of lead containing a small quantity of dioxide

C S

On J. C. A. Bock's Process for the Production of Stearic and Palmitic Acids. By W L CARPENTER (Chem Centr, 1872, 744) —This process consists in treating the fat with a small quantity of sulphuric acid, and subsequently decolorising the fat acid by means of oxidising agents

W A T

Manufacture of Rosaniline. By A BRUENING (Deut Chem Ges Ber, vi, 25) —This new and practical method consists in the action of (commercial) nitrobenzene on magenta-aniline

C S

The Crystalline Precipitate produced in Beer on the addition of Potassium Carbonate. By A MEIZ (Chem Centr, 1872, 558) —The addition of potassium carbonate to beer gives rise to the formation of small crystals which adhere to the sides of the vessel in which the precipitation takes place The best results were obtained by heating a litre of the beer to the boiling temperature and adding 10 grams of potassium carbonate dissolved in a small quantity of water The crystals were analysed by the author and by Griessmayer, and were found to consist of potassio-magnesium phosphate, $MgK_2P_2O_8 + 6H_2O$

T B

A Collodion of Extraordinary Tenacity. By R BOTTGER (Chem Centr, 1872, 745) —Collodion cotton is dissolved in a mixture of equal volumes of ether and absolute alcohol and a small quantity of balsam of copaiva added Spread on glass, it leaves a membrane of extraordinary firmness

W A T

Newly discovered Property of Gun-cotton. (Dingl polyt J, ccvi, 500)—A notice of Brown's observation that it is possible to explode compressed gun-cotton even when wet

C H G

The application of Carbon Sulphide to the freeing of Wool

from Fats. (Dingl. polyt. J., ccvi, 502.)—Though the fat is easily removed by this reagent, it is found that the wool is rendered so yellow and brittle that the process is not worth working. It is suggested in the paper that the carbon sulphide unites with and alters the sulphuretted constituent of the wool.

C. H. G.

Tracing Paper. (Dingl. polyt. J., ccvii, 86.)—Castor-oil is mixed with 3 or 4 parts of absolute alcohol, and the homogeneous mixture spread over paper with a brush. By washing with alcohol, the oil is again dissolved, and the paper restored to its original character.

M. M. P. M.

Changes in the Sugar of Beets. (Dingl. polyt. J., ccvii, 88.)—Pasteur's researches have shown that beet-sugar in an atmosphere of carbon dioxide undergoes the lactic fermentation, part of the sugar being destroyed, and part converted into non-crystallisable sugar. He has also shown that when the beets grow mouldy, they exhale carbon dioxide if, therefore, they are kept for any length of time before the sugar extracted, they will be in those circumstances under which this sugar is so easily decomposed. The beets should be kept in a well-ventilated place, but even here they must not remain longer than is absolutely necessary.

M. M. P. M.

Griessmayer's Hop Extract. (Chem. Centr., 1873, 105.)—In this paper are set forth:—

1stly. The desirability of a process for preparing a good hop-extract, so that the excess of hops obtainable in an exceptionally rich hop-harvest may thus be utilised and kept in the form of extract to compensate for years of scarcity.

2ndly. The difficulties hitherto standing in the way of processes devised for the preparation of the extract.

3rdly. That a process has been recently discovered which is successful in every respect; but unfortunately the "modus operandi" is kept secret.

W. S.

The Free Acids in Wine. By Graeger (Chem. Centr., 1873, 105).—Old wines have an acid reaction, in consequence of the presence of a certain amount of free acid and potassium bitartrate. A wine not exhibiting this acid reaction tastes flat; the acidity is its most important flavour. For a long time it has been believed that the free acid of wine is tartaric acid alone. Nessler's researches have, however, shown that this is seldom the case, frequently tartaric and malic acids existing together, and more frequently the free acid consisting of malic acid entirely. Wines containing tartaric acid alone taste more tart than those with only malic acid, or a mixture of malic and tartaric acids. Nessler shows that only in rare cases does the free acid in grapes consist solely of tartaric acid; in most cases a mixture of malic and tartaric acids is present in variable proportions.

W. S.

The Treatment of Wine with Air during Fermentation. By Adolph Ott (Dingl. polyt. J., ccvii, 155—161, from Engineering and Mining Journal, July, 1872).—The process consists in driving air through the fermenting liquor, at a temperature of 26°—27° C., for half an hour on the first day, and for several minutes on each succeeding day till fermentation is complete, which requires from five to fourteen days. The wine can be drawn off from the yeast in a few days after, and in one or two months will be quite clear, free from any tendency to secondary fermentation, and of a more agreeable flavour than wine fermented in the ordinary way and kept for two years.

The method is due to D'Henreuse, of San Francisco.

C. H. G.

Combustible Boiler Crust. (Dingl. polyt. J., ccvii, 81.)—This crust formed in the boiler of a manufactory in Chicago. It contained 20·92 per cent. organic matter; 16·04 fat extracted by benzol.; 63·04 ash. The addition of a little soda obviates the formation of this crust.

M. M. P. M.

On the Continuous Distillation of Petroleum, Mineral Oils, &c., at Constant Levels, and with Fractional Condensation. By H. Fubst (Dingl. polyt. J., ccvii, 293—304).

Fire-resisting Qualities of various Building Stones. By A. Ott (Dingl. polyt. J., 310—313).

Asphalt, its Extraction, Preparation, and Uses. By L. Bideky (Dingl. polyt. J., ccvii, 240—253 and 328—337).

On Spontaneous Combustion, with reference to its Prevention in Flour Mills. By A. Kühl (Dingl. polyt. J., ccvii, 367—378).

On the Importation of Preserved Meat. By H. Senfleben (Dingl. polyt. J., ccvii, 417—423).

On Machinery and Constructions for the Bessemer Process. By E. F. Düzze (Dingl. polyt. J., ccvii, 394—400).

Utilisation of Waste Soap-waters. By F. Heuze (Dingl. polyt. J., ccvii, 463).

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXVI.—*On Smelting Iron and Steel.*

By C. WILLIAM SIEMENS, D.C.L., (OXON,) F.R.S.

[A Lecture delivered before the Chemical Society, March 20th, 1873]

ON the 7th of May, 1868, I had the honour of addressing you on the subject of "the regenerative gas furnace* as applied to the manufacture of cast steel," my object being at that time to point to the important part which that furnace was likely to play in such metallurgical processes where intense heat is required. At that time I described a method of producing cast steel upon the open hearth of a regenerative gas furnace by the dissolution either of scrap iron or of ores in a more or less reduced state in a bath of intensely heated pig metal. These processes have now received very considerable practical development at the works of the Landore-Siemens Steel Company, of Messrs. Vickers and Company of Sheffield, and at several other works. Two processes are employed at these works, the Siemens-Martin process, which consists in dissolving scrap metal or steel in a bath of pig metal to which spiegeleisen is finally added, and the ore-reducing process in which pig metal, and ore in a more or less reduced condition is employed.

The process chiefly employed at the Landore works consists of introducing on the bed of an intensely heated regenerative gas furnace, as shown in Figures 1 and 1*a*, about 6 tons of pig metal, which may be No. 3 or 4 hæmatite pig. When a fluid bath has been formed, oxide of iron (which should by preference have been melted before-hand with such proportions of lime or other fluxing materials as to form with the silica in the ore and in the pig metal a convenient slag) is added, or natural ores may be used in their raw condition if they contain lime and manganese, as for example, the African Mokta ore. When about 30 cwt. of this ore have been dissolved (with ebullition) in the metallic bath, it is found that a sample taken from it contains only about ·1 per cent. of carbon; a point which can easily be detected by the eye of the workmen by a peculiar bright appearance of the sample when chilled in water and broken by the hammer.

In order not to pass beyond this point, samples are taken out from time to time during the latter part of the operation, and such a series of samples, which have been kindly supplied to me by Messrs. Vickers and Co., together with samples of steel made by the process, are now

* The joint invention of C. William and F. Siemens.

placed before you. When the requisite point of decarburisation has been reached, the supply of ore must be stopped, and from 8 to 10 per cent. of ferro-manganese or spiegeleisen added to the bath. When this has been well incorporated by stirring, the metal is ready to be tapped into a ladle mounted upon wheels, which is afterwards propelled into the foundry, and discharged either into ingot moulds, to be hammered and rolled, or into dried clay moulds for the production of steel castings.

Considerable difficulty was experienced to find a material to resist the excessive heats necessary for carrying out this process; ordinary Dinas bricks, which are considered the most refractory material in general use, would be rapidly melted, but a brick, specially prepared by crushing pure quartz rock, and mixing it with no more than 2 per cent. of quick lime to give cohesion, answers well. The hearth of the furnace is made of white sand with a small admixture of more fusible fine sand, which mixture sets exceedingly hard at a steel-melting heat, and possesses the advantage of combining into a solid mass with fresh materials introduced between the charges to make up for wear and tear. The hearth and the furnace roof if of the materials just specified, are very little attacked when the Siemens-Martin process is used, although the heat must be sufficient to maintain wrought iron containing only a trace of carbon, in a perfectly fluid condition. If pig metal, and ore (fused together with the necessary amount of flux) is used, the furnace also stands well, but the use of raw ore entails the disadvantage of a more rapid destruction of the furnace; even magnetic oxide of the purest description necessitates the addition of raw lime for the formation of a fusible slag, and the dust arising from the lime and through the decrepitation of the ore causes the silica bricks to melt away rapidly, so that after perhaps two months' usage, the 9-inch arch of the furnace is reduced to the thickness of from 1 to 2 inches. It is evident that silica is chemically speaking an objectionable material to be used in the construction of these furnaces, because it prevents the formation of basic slags, and that a furnace constructed of pure alumina or lime would be preferable. My friend M. Le Chatelier, Inspecteur-Général des Mines, whose valuable labours for the advancement of iron metallurgy are well known, suggested to me years ago the use of Bauxite (from Baux in France, where it was first discovered), a mineral consisting chiefly of alumina, for making the furnace-bed, but I was not able to succeed with this owing to the great contraction of the mass when intensely heated, and non-cohesion with the same material introduced for the purpose of repair. In attempting to construct the sides and roof of the furnace of Bauxite bricks, these were not found to be equal in heat-resisting power to silica bricks, which latter are indeed unobjectionable, except when raw ore and limestone are used.

If good pig-metal, such as is used in the Bessemer process is employed, a metal of high quality is the result, equalling in most respects the steel produced by melting Swedish bars in pots by the old Sheffield process.

There is manifestly an analogy between this and the Bessemer process, both of them being processes of decarburisation of pig metal; yet there are very important differences, both as regards the nature of the chemical reactions and of the metal produced. In the Bessemer process the silicon and carbon are fully oxidised by the action of the blast, whereas sulphur and phosphorus are known to remain unoxidised. Manganese is oxidised in the Bessemer process only to a certain extent, and therefore it is not necessary to add spiegeleisen at the end of the operation, when the pig metal employed contains a moderate amount of metallic manganese, as is the case in Sweden and in Styria. Mr. W. Hackney, the manager, and Mr. A. Willis, the resident chemist at the Landore Steel Works, have analysed Bessemer metals made without the final addition of spiegel, and found them to contain no less than 0·3 per cent. of manganese. Notwithstanding the non-oxidation of manganese, from 8 to 10 per cent. of iron is oxidised in the Bessemer process, although iron has naturally less affinity to oxygen than manganese. The oxidation of this amount of iron in the Bessemer converter is, in so far, a fortunate circumstance, as without it the amount of heat necessary to liquefy the resulting malleable iron could not be produced, and the metal would necessarily set in the converter. In the ore-reducing process above described a totally different result ensues, as is shown by the following experiment.

A manganiferous pig was melted, and ore charged in the usual manner. After the pig was completely melted, it contained the ingredients stated in the first line of the following table, from which it will be seen that silicon and manganese were eliminated first, and then very little change took place in the carbon until the two other constituents were completely removed:—

Samples taken	Contained		
	Carbon.	Silicon.	Manganese.
When pig was melted..........	1·90	·57	1·14
1 hour later..................	1·8	·233	·576
2 hours later	1·7	·183	·2
3 " "	1·65	·05	·08
4 " "	1·6	none	none
5 " "	1·1	Manganese and silicon completely gone.	
6 " "	·6		
7 " "	·2		

The sulphur and phosphorus are oxidised to a considerable extent; a circumstance which enables us to use pig metal containing a certain small percentage of these admixtures, which are not absolutely objectionable unless they occur in excessive proportions, the quantity admissible of both phosphorus and sulphur being about ·08 per cent.

The decarburising agent employed being ferric oxide, no cast-iron can possibly be oxidised, and a ton of pig metal with its quota of spiegel containing from 9 to 10 per cent. of foreign substances, yields fully 21 cwt. of steel ingots. In this process the addition of spiegeleisen at the end of the operation is an absolute necessity, however much manganese may have been contained in the pig metal employed, because the manganese is rapidly oxidised, as can be seen from the foregoing table.

The reason of the different reaction in the Bessemer process is, in my opinion, that the silica liberated from the beginning of the operation requires a base for its saturation, and that its great affinity to protoxide of iron determines the oxidation of this metal (free oxygen from the blast being present) in preference to manganese.

A characteristic difference between the two metals, in their fluid condition, is that Bessemer metal on cooling in the moulds sets up a violent ebullition, probably resulting from a reaction between occluded oxygen and carbon, which is counteracted by stoppering the moulds. The ore process metal, if it has been made with care, on the contrary, contains no occluded oxygen, and sinks in the moulds on cooling in the same way as "dead melted" steel does produced by the old Sheffield process.

It has been an open question between metallurgical chemists whether manganese is really required to be present in malleable steel, some maintaining that its beneficial action is confined to the elimination of sulphur during the process of production. Such, however, is not the case, as may be seen from the following extract from Messrs. Hackney and Willis's report:—

"Our observation, based on five years' experience, is that no chemical reaction takes place between the manganese of the spiegeleisen and the other elements of the steel, but that it acts simply as an alloy. With regard to manganese not removing any sulphur in a bath of steel, it is a curious fact that the reverse takes place in a blast furnace. As the percentage of manganese in the pig increases, so does the sulphur decrease; for instance, if to ore and coke, which in the ordinary way will produce a pig containing from 2 per cent. to 3 per cent. of sulphur, manganiferous ore is added so as to put 2 per cent. of manganese into the pig, the sulphur will be reduced to ·05 or ·08 per cent.; but when 3 per cent. of manganese is found in the pig it never contains more than a slight trace of sulphur. We have had occasion lately to analyse several hundreds of samples of pig iron made under these conditions,

and can vouch for the accuracy of this statement, and we think it a fact well worth the attention of ironmasters who are troubled with an excess of sulphur either in their ores or fuel.

"Every one must have noticed the absence of sulphur in all analyses of spiegeleisen, although much of it is made from coke, and most of the ores used contain a considerable quantity of pyrites.

"That the manganese acts by its actual presence, and not by any chemical reaction, is, we think, proved by the fact that, if through any accident or carelessness of the workmen, the charge is left in the furnace for more than twenty minutes after the spiegeleisen is fairly melted the steel is invariably bad, owing to the oxidation of the manganese, and therefore if such delay occurs, a small addition of spiegeleisen is made, and no bad results follow."

About the impurities of steel the same gentlemen report :—

"The presence of sulphur, it is well known, makes steel red-short, and the only question is, how much may it contain without injury? Our experience is, that up to ·08 per cent. will do no harm provided there is also present 3 per cent. of manganese, and I have even found ·112 per cent. without having any complaint from the hammermen.

"Phosphorus does not appear to affect either the rolling or hammering of steel, even if 2 per cent. is present, but if it exceeds 0·8 per cent., the rails become so cold-short that they will not stand the severe test to which they are subjected.

"The presence of arsenic and phosphorus increases the hardness of steel at the expense of its toughness.

"The effect of copper is not yet understood; according to Percy it renders steel red-short to a greater extent even than the same amount of sulphur.

"From the nature of the process, as a rule, very little if any silicon is found in Siemens' steel. The carbon and silicon appear to be eliminated equally when manganese is not present, and, as the carbon is generally in excess of the silicon, none remains when the carbon is reduced to 2 per cent. The small amount found in the steel is derived from the spiegeleisen."

At the Landore Works upwards of 1,000 tons of cast steel are produced weekly by these processes, and other works, such as Vickers and Company, Krupp, of Essen, etc., are using the same for the production of steel of high quality.

Both in the ore-reducing and in the Siemens-Martin or scrap process, pig metal forms the principal basis, being used either as such, or as puddled iron or Bessemer scrap-metal, resulting from the conversion of pig metal by a previous process.

In my former lecture I expressed my belief that the direct conversion

of ores into iron or steel would ultimately be accomplished, and, having since been actively engaged on the problem, it is now my chief object to lay before you the results I have up to this time attained.

I am aware that, on the one hand, the direct conversion of iron ores into wrought iron or steel is no novelty, inasmuch as the ancient Indians and Romans produced their iron by a direct process from the ore; and that, on the other hand, the blast furnace offers immense facilities for the wholesale extraction of metal from the ore, by the side of which the puny efforts of the ancients producing half a cwt. of metal intermixed with half-fused cinder by a day's toil, and with the expenditure of large quantities of rich ore and charcoal, sink into utter insignificance.

Mr. Riley says, in his able lecture "On the Manufacture of Steel and Iron," read before this Society on May 22, 1872:—

"The great improvement lately introduced in the manufacture of pig iron, the enormously increased production at a diminished cost of what may be considered to be the raw material from which we start in the manufacture of iron and steel, are, I think, sufficient to convince not only practical men, but scientific men also, that in any improvement in iron manufacture we must commence with the pig, and consider that our starting point."

Mr. Riley here gives expression to the prevailing opinion amongst metallurgists; but still I do not despair of being able to prove to you that upon theoretical grounds the blast furnace is open to very grave objections, inasmuch as it produces iron combined with nearly all the objectionable substances contained in the materials used, that only expensive fuel, such as coke, can be employed, and that its combustion is necessarily imperfect.

The accompanying figure (Fig. 2) shows the distribution of temperature in the blast furnace, as given by Mr. Lowthian Bell in a paper read by him before the Institution of Civil Engineers, in 1872. It shows that the reduction of the metallic oxides to spongy iron is accomplished within the first 20 feet of their descent in the furnace, and at a comparatively low temperature. This upper zone is followed by one where the limestone is decomposed and the carburisation of the spongy metal is commenced. Between this second zone and the zone of fusion in the boshes of the furnace a zone of great magnitude intervenes, where apparently no other change is effected than an increase of temperature of the spongy metal, but where in reality a very powerful reducing action is accomplished of substances which had much better not be joined to the iron. It is well known that almost all the phosphorus contained in the iron-stone, the lime-stone, and the coke is here incorporated with the spongy iron. The silica is reduced to its metallic condition, and, together with sulphur, arsenic, and other bases which

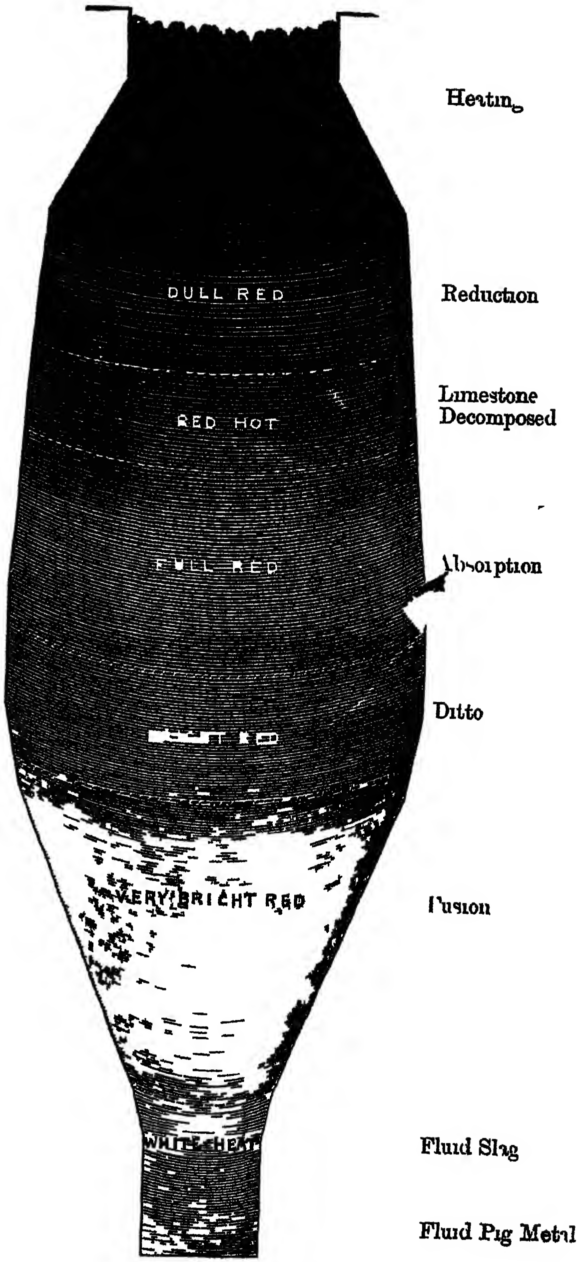


FIG. 2—BLAST FURNACE.

may be present, combines with the iron. The final action in the blast furnace consists only in fusing those reduced substances and forming the slags which envelop and protect the fused metal.

As regards the fuel question, it will be observed that the result of the combustion in the blast furnace is for the most part carbonic oxide, and that the heat developed in this combustion amounts to only 2,400 heat units per pound of pure coke consumed, whereas a perfect combustion (to carbonic acid) of the same coke would be attended by the development of 8,000 heat units. It is practically impossible to obtain more than one-fifth of carbonic acid to the carbonic oxide issuing from the top of the blast furnace, and it may, therefore, fairly be asserted that only one-third of the heat-producing power residing in the coke is utilised in this furnace. A portion of the heat thus left undeveloped may be used, it is true, in burning the gases for the generation of steam or for heating the air blown into the blast furnaces; but this utilization represents only a small proportion of the value of the coke or charcoal charged with the ore into the furnace; whereas a much cheaper material might be employed for the purposes just named. The introduction of hot blast was unquestionably a very great improvement in blast furnace economy, because the heat thus introduced is obtained by means of the perfect combustion of fuel, and, in reducing the combustion necessary within the furnace, the quantity of products of combustion as compared to a unit quantity of ore is greatly reduced, the effect being that the incoming ores have a relatively greater capacity for absorbing the sensible heat from the products of combustion, which latter must therefore issue from the top of the furnace at a lower temperature.

Relying upon this argument, I am inclined to believe that the consumption of coke in a blast furnace must materially diminish with increased temperature of blast without limitation of degree, and in this respect I venture to differ from my friend Mr. Lowthian Bell, who maintains that mere increase of capacity of furnace up to a certain limit produces the same effect as increase of temperature of blast, and that no beneficial effect can be obtained by increasing the temperature of blast beyond 515° C. In taking, however, the best examples of blast furnaces, the products of combustion escaping from the top, four parts out of five, as CO without counting the N and at not less than 350° C. of sensible heat, carry with them fully two-thirds of the heat they would be capable of producing, if they were burnt to carbonic acid.

In my former lecture I described a plan of reducing iron oxides by feeding them, mixed with carbonaceous materials, into a reverberatory furnace through inverted hoppers of fire-clay, the intention being to effect the reduction of the iron ores into spongy metal during their descent, and the fusion of the spongy metal so produced on the open hearth of the furnace, pig metal being used to facilitate the fusion. It

was found, however, that the quantity of heat that had to be transmitted through the sides of the fire-clay hopper was so great that the process of reduction proceeded very slowly, and the hoppers themselves were rapidly destroyed by the intense heat of the furnace. The time necessary for the reduction of the metallic iron in closed chambers of this or any other form which I have tried cannot be effected in less than about 36 hours, and that at a great expenditure of fuel for heating the chamber externally.

This unsatisfactory result directed my thoughts to another method of producing spongy iron by means of a rotative furnace. This furnace consisted of a long cylindrical tube of iron of about 8 feet diameter, mounted upon antifriction rollers; the brick lining of it was provided with longitudinal passages for heating currents of air and gas prior to their combustion at the one extremity of the rotating chamber. The flame produced passed thence to the opposite or chimney end, where a mixture of crushed ore and carbonaceous material was introduced. By the slow rotation of this furnace the mixture advanced continually to the hotter end of the chamber, and was gradually reduced to spongy iron. This dropped through a passage constructed of refractory material on to the hearth of a steel-melting furnace, where a bath of fluid pig metal had been provided. The supply of reduced ore was continued till the carbon in the mixture was reduced to the minimum point before indicated. The rotation was then arrested to prevent further descent of reduced ore; spiegel was added; and the contents of the melting furnace tapped into a ladle and thence into ingots, as before described.

This rotary furnace was erected by me at the Landore Works in 1869, and it was so far successful, as the reduction of the ore was accomplished in a comparatively short time. A difficulty, however, presented itself, which led to its immediate abandonment; it was found that the spongy metal produced absorbed sulphur from the heating gases, and was rendered unfit for the production of steel; the spongy iron moreover, upon its introduction into the steel-melting furnace, floated upon the metallic bath without being readily absorbed into it, and was in great part reoxidised and converted into slag by the action of the flame in the furnace.

These experiments convinced me that the successful application of reduced ores could not be accomplished through their conversion into spongy metal, and fully explained to me the want of success which has attended the previous efforts of Clay, Chenôt, Yates, and others, to produce iron directly from the ore. On the other hand, I had observed that in melting iron ores no sulphur was absorbed from the flame; and it occurred to me that by melting ores mixed with fluxing materials in a furnace so arranged as to accomplish its fusion in a continuous

manner, and on a large scale, the fused ore might be acted upon by solid carbonaceous matter, so as to separate the metallic iron in a more compact form, while the earthy constituents of the ore would form a fusible slag with the fluxing material. Experiments proved that this reduction by precipitation of the iron could be accomplished only at an intense heat, exceeding the welding heat of iron, but that the iron so produced was almost chemically pure, although the ores and the fuel used might contain a very considerable percentage of sulphur and phosphorus. The specimens of iron which I exhibit were made in this manner from ores of various descriptions, and the following tables give the analysis of the ores and the iron, as also the yield of iron obtained from a ton of ore:—

Results of Precipitation Process at Landore.

Ores	Charge.		Yield.
	Total.	Coal charged in furnace.	
Mokta ore ....12 cwt. Scale .... 8 „	20 cwt.	6 cwt.	14 cwt.
Mokta ore ....10 „ Scale .... 8 „	18 „	4 „	14 cwt 2 qrs.
Mokta ore ....12 „ Scale .... 8 „	20 „	6 „	11 „ 2 „
Mokta ore .... 6 „ Scale .... 4 „	10 „	2 „	12 „
Mokta ore ....10 „ Scale ....10 „	20 „	6 „	15 „ 2 „
Mokta ore ....14 „ Scale ....12 „	26 „	6 „	18 „
Total................	114 cwt.	30 „	85 „ 2 „

Results of Rotator.

	Ore.	Lime.	Coal.	Iron.
Vickers, Sheffield........	984	48	216	492
„ Birmingham....	784	40	176	258

Results of Precipitation Process at Blochairn.

Charge.						Yield of iron.	Analysis of iron. Impurities.
No.	Ores.	Lbs.	Total.	Lime.	Coal.		
1	Purple .... Red	450 150	600	56	356	137	S = 055 per cent. P = 114 " Si = ·13 "
2	Purple .... Red	168 56	224	12	170	165	
3	Melted .... Coke (powder) ..	350 210	560	—	—	160	
4	Purple .... Blackband......	300 600	900	90	390	210	
5	Blackband...... Clayband ...... Purple	600 600 300	1500	150	420	210	
6	Blackband...... Clayband ...... Purple	300 300 300	900	90	145	202	
7	Cleveland ...... Purple	900 300	1200	120	290	268	S = 011 per cent. P = 150 " Si = 173 "

Working Results of the Cascade Furnace at Landore.

Charge in cwt.				Yield.	
Mokta ore.	Roll scale.	Roll scale.	Coal.	Puddled bar.	
				cwt.	qrs.
8	8	16	4	7	2
10	8	18	3	15	
6	6	12	3	8	
4	8	12	4	11	
10	8	18	6	13	
6	4	10	2	12	
12	8	20	6	14	
10	8	18	4	14	2
12	8	20	6	11	2
10	10	20	6	15	2
14	12	26	6	18	
102	88	190 cwt.		140	

The ore employed was Mokta ore, of the following description:—

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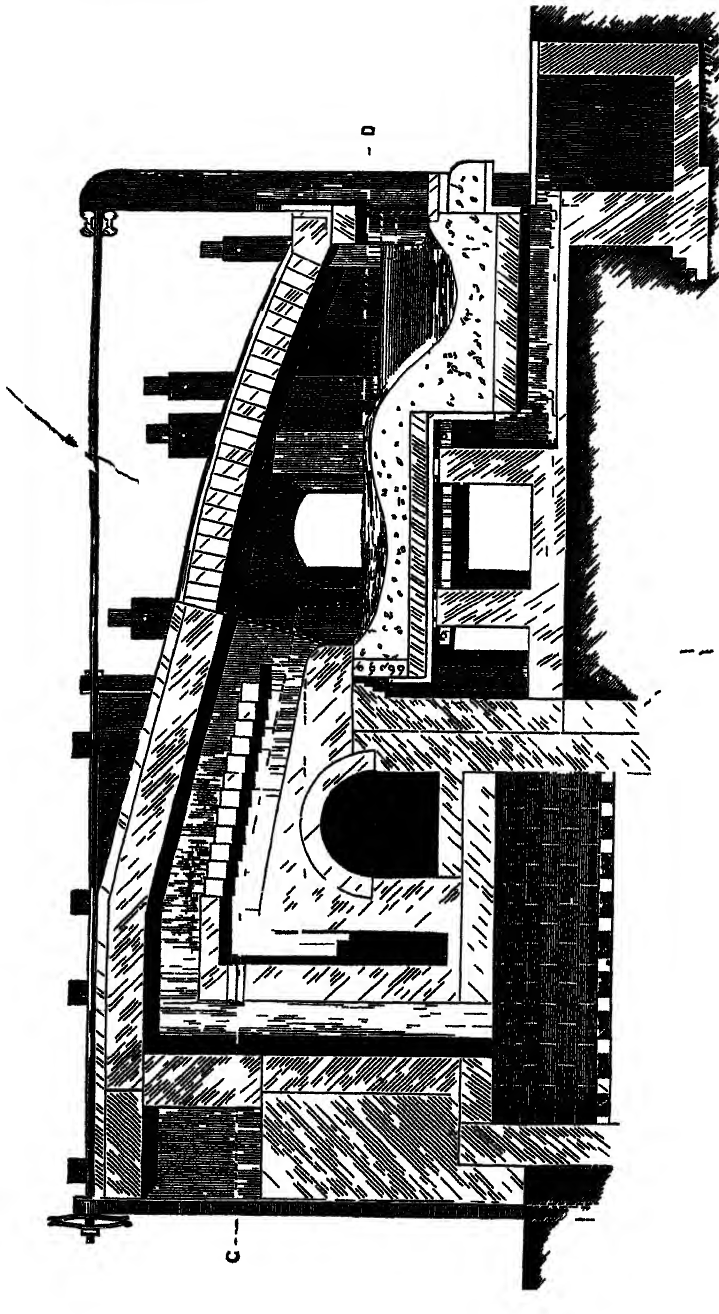


FIG 3 LONGITUDINAL SECTION OF CASCADE FURNACE

Fe_2O_3	79 74	Fe 60 8
FeO	6·43	
Mn_3O_4	2 92	
CaO	·52	
MgO	·25	
SiO_2	4·75	
Loss on ignition......	5·11	
	99·72	

	Yield	Lbs. slabs.
32 charges, 14,338 lbs. ore....		
„ 5,952 „ coal ..	8,115 =	56·6 per cent.
„ 768 „ lime ..		

Other specimens of steel shown are produced by fusion of the iron thus obtained in the open hearth of a regenerative gas furnace, which are undoubtedly of superior quality.

The furnace used for carrying out this process of fusion and precipitation is shown by the accompanying Figures 3 and 3*a*. It consists of a reverberatory gas furnace having two beds formed by the ore itself; on the upper bed a lake of fused ore is formed which can be let off into the lower bed by piercing the intervening bank of unfused ore; the lower bed is divided into two compartments, each provided with a working door, used alternately. The dense carbonaceous material, such as anthracite or hard coke, to be used for the precipitation of the iron in the lower bed, is reduced to a state of powder and mixed with about an equal weight of pulverulent ore. This mixture is spread over the bottom surface of the working bed and the fluid ore is let in upon it. By stirring with a rabble it is transformed into a pasty and foaming mass, which in the course of from 40 to 50 minutes is shaped into a metallic ball in a bath of fluid cinder, which may be shingled in the usual manner and formed into bar iron or transferred to the pig-iron bath of a steel-melting furnace, where it readily dissolves. The accomplishment of this process involves, however, a certain degree of manual labour and skill, as, if it be carelessly conducted, the yield of iron will be unsatisfactory; the analysis of the slags shows a variable percentage of iron amounting rarely to less than 15 per cent., but reaching occasionally up to 40 per cent.

It was evident that if iron and steel were to be produced largely by direct process, that process must be a self-acting or mechanical one, and here my attention again reverted to the rotating furnace above mentioned. If I could succeed in furnishing such a rotating furnace with a lining capable of resisting the high degree of heat requisite for the precipitation of the iron, and at the same time capable of resisting the

chemical action, I felt confident that this mode of conducting the process must succeed. My attention here reverted to M. Le Chatelier's former suggestion of the use of Bauxite, which possesses the requisite qualities, if only it can be put into a compact form and rendered sufficiently infusible.

A series of experiments to form solid lumps by using different binding materials have shown that 3 per cent. of argillaceous clay suffice to bind the Bauxite powder previously calcined. To this mixture about 6 per cent. of plumbago powder is added, which renders the mass practically infusible, because it reduces the peroxide of iron contained in the Bauxite to the metallic state. Instead of plastic clay as the binding agent, waterglass or silicate of soda may be used, which has the advantage of setting into a hard mass at such a comparatively low temperature as not to consume the plumbago in the act of burning the brick. When the lining is completed, the interior of the bricks is preserved against oxidation by fluid cinder, added to bind them together, which prevents contact with the flame. A Bauxite lining of this description resists both the heat and fluid cinder in a very remarkable degree, as I have proved by lining a rotative furnace at my Sample Steel Works at Birmingham, partly with Bauxite and partly with carefully-selected plumbago bricks. After a fortnight's working the brick lining was reduced from 6 inches to less than half an inch; whereas the Bauxite lining was still 5 inches thick and perfectly compact. It is also important to observe that the Bauxite when exposed to intense heats is converted into a solid mass of emery of such extreme hardness, that it can hardly be touched by steel tools, and is capable of resisting mechanical as well as the calorific and chemical actions to which it is exposed. The Bauxite used for this lining was of the following composition:—

Alumina	53·62 per cent.
Peroxide of iron	42·26 "
Silica	4·12 "

Other Bauxites which I have had occasion to analyse were composed as follows:—

Analysis of various Bauxite.

FRENCH BAUXITES.—FIRST GROUP.

	SiO_2.	Al_2O_3.	Fe_2O_3.	H_2O.
	1·7	66·2	19·7	12·7
	4·2	54·2	28·7	13·0
	3·7	58·9	25·7	12·4
	3·2	55·9	28·1	12·2
	3·2	60·4	25 1	11·5
	3·9	56·4	22·1	13·5
	3·2	61·2	23·1	11·3
	5·9	58·8	23·1	11·3
	2·8	60·7	25·3	11·8
Average Raw ..	3·5	59·2	24·5	12·1
Average Calcined	4·01	67·89	28·09	

SECOND GROUP.

	SiO_2.	Al_2O_3.	Fe_2O_3.	H_2O.
	2·4	52·5	29·0	15·0
	2·5	41·8	43·7	13·0
	1·7	25·2	53·5	10·05
	2·1	38·7	50·2	11·8
	1·4	38·7	48·5	12·0
	1·1	39·2	40·3	9·4
	1·0	38·7	48·0	12·5
	1·9	41·2	41·7	15·9
Average Raw ..	1·75	39 5	45 5	12·57
Average Calcined	2·02	45·53	52·45	—

AUSTRIAN BAUXITE.—WOCHEINITE (CARNIOLA.)

	Raw.	Calcined.
Al_2O_3	64·24	85·88
Fe_2O_3	2·40	3·20
SiO_2	6·29	8·40
CaO	·85	1·13
MgO	·38	·50
SO_3..........	·20	·26
PO_4..........	·46	·51
H_2O	25·74	—

IRISH BAUXITE.

	Raw.	Calcined.
Al_2O_3	35 0	44·58
SiO_2	3·5	4·45
TiO_2	2·0	2·54
Fe_2O_3	38·0	48·40
H_2O	21·5	—

Figures 4, *4a*, *4b*. *4c*, and *4d* represent the complete rotary furnace, such as is now in use at Messrs. Vickers and Co.'s, at Sheffield, and at my Sample Steel Works at Birmingham. It consists of a set of four regenerators of the usual construction with reversing valves and gas producers, which latter are not shown. The rotative chamber is constructed of iron, and rests upon four anti-friction rollers. Wheel-gearing is applied by which either a very slow rotative velocity of from four to five revolutions per hour can be imparted to the chamber, or a e rapid velocity of about 60 to 80 revolutions per hour. The ber is about 7′ 6″ in diameter and 9′ 0″ long, and is provided with a te lining about 7″ thick. A tap-hole is on the working side for

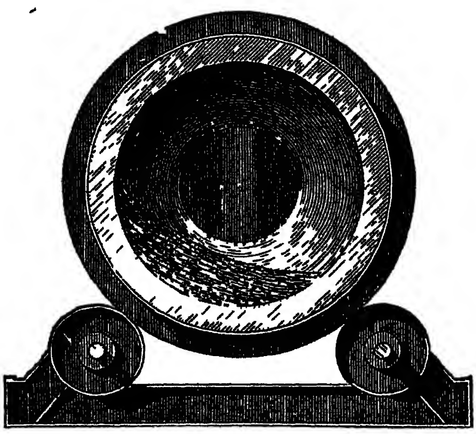


FIG. *4d*—SECTION THROUGH ROTATOR.

discharging the slag into the cave below, where it is received in vessels mounted on wheels. At the two extremities of the cylindrical rotative chamber with its truncated ends, are large orifices, one of which, on the side of the regenerators, serves for the introduction of the heated gas and air as well as for the exit of the products of combustion, and the other facing the working platform is closed by a stationary door hung before it in the usual manner. Although the passage for the

regenerators, and completes with it perfect combustion within the free space of the chamber. The carbonic acid thus generated comes in no further contact with carbon, consequently it cannot split up, but is drawn away unchanged into the chimney, while the evolved heat is taken up by the sides of the chamber and transmitted by reverberation and conduction to the mixture of ore, fluxes, and coal.

In this process we have, therefore, to accomplish two things, viz., the deoxidation of the ore, and the fusion of the earthy matter mixed with it. If we take (say) hæmatite ore, consisting of peroxide of iron with 10 per cent. of silica, we shall determine the quantity of carbon necessary for its reduction from the formula

$$Fe_2O_3 + 3C,$$
$$\text{which gives } 2Fe + 3CO;$$

and according to which the consumption of carbon (taking its atomic weight at 12 and that of iron at 56) amounts to

$$\frac{3 \times 12}{2 \times 56} = \cdot32 \text{ lbs. per lb. of iron reduced.}$$

The heat absorbed in this reaction amounts, according to Dr. Debus, to 892 units* per lb. of iron produced, but on the other hand the further combustion of ·32 lb. of carbon from the condition of carbonic oxide to carbonic acid, or from CO to CO_2, by means of the free oxygen introduced into the rotative chamber from the regenerator yields

$$\cdot32 \times 5600 = 1792 \text{ units of heat}$$

leaving

$$1792 - 892 = 900 \text{ units}$$

available for heating the materials and for melting the slag.

The quantity of materials to be heated per lb. of iron produced would amount to

Ore..............................	1·59
Lime or other fluxing materials....	·16
Total....................	1·75

and taking the specific heat of Fe_2O_3 at ·154 as determined by Herman Kopp, and the temperature to which the materials have to be raised at 1500° C., the heat required for this purpose would not exceed

$$1{\cdot}75 \times \cdot154 \times 1500 = 403{\cdot}5 \text{ units.}$$

To this consumption would have to be added the latent heat absorbed in liquefying the slag. This would amount to ·32 pound per lb. of iron produced, and, although we have no precise data from which we

* Dr. A. W. Williamson gives 885·3 units as the result of his calculation, which two figures agree sufficiently for my present purpose.

could ascertain the latent heat absorbed in liquefaction, we can hardly estimate it at more than 400 units per lb., or at $\cdot 32 \times 150 = 88$ units, which, with the above 403·5, makes 451·5 units or 448·5 units under the 900 heat-units which are available, proving that ·32 lb. of pure carbon would, theoretically speaking, amply suffice to produce 1 lb. of puddled bar from ordinary hæmatite ore, without counting however losses of heat by radiation and from other causes.

In the production of cast steel, three operations are essentially involved, viz., the deoxidation of the iron, the fusion of the slags, and the fusion of the metal itself with such proportion of carbon and manganese as is necessary to constitute steel of the temper required.

The theoretical quantity of fuel required to accomplish these operations would exceed that of making wrought iron by the fusion of heated metal, which may be estimated at, say 1000 units, or at $\frac{1000}{8000}$ $=$ ·125 lb. of carbon per lb. of steel produced, which have to be added to the ·32 lb. used in reduction.

In fine, a ton of iron ought to be producible from hæmatite ore with 6·4 cwt. of carbonaceous matter, or say 8 cwt. of common coal, and a ton of cast steel with 8·91 cwt. of carbon, or say 11 cwt. of coal. In giving these figures, I do not wish to imply that they will ever be completely realised, but I maintain that, in all our operations, we should fix our eyes upon the ultimate result which theory indicates, which, owing to the imperfect means at our command, we shall never completely realise, but which we should constantly endeavour to approach.

In taking incidental losses by radiation through imperfect combustion and through imperfect absorption of heat into account, we find that the actual consumption exceeds the theoretical limits about three times, or that a ton of iron can practically be produced with a consumption of 14 cwt. of coal, and a ton of cast steel with 12 cwt. of coal, which consumption represents a great reduction as compared with other methods of production.

XXVII.—*Researches on the Action of the Copper-zinc Couple on Organic Bodies.*

Part II. *On the Iodides of Amyl and Methyl.*

By J. H. Gladstone, PhD., F.R.S., and Alfred Tribe, F.C.S.

Frankland found that "iodide of amyl is acted upon by zinc with much more difficulty than the corresponding ethyl compound;"* he speaks of the necessity of "a very nice management of the tempera-

* Chem. Soc. J., iii, 81.

ture," and though he mentions zinc-amyl among the results of the reaction, he never obtained it in any quantity by this method. For the decomposition of iodide of amyl he resorted to the use of zinc-amalgam in powder in sealed tubes at a temperature a little above that of the boiling-point of the liquid. He thus obtained, not zinc-amyl but a mixture of three hydrocarbons, viz., amyl, $C_{10}H_{22}$, a light liquid boiling at 155°; hydride of amyl, C_5H_{12}, an exceedingly mobile liquid with an agreeable odour, boiling at 30°; amylene, C_5H_{10}, another limpid liquid boiling at 35°, and combining with fuming sulphuric acid.

It appeared to us therefore a point of special interest to ascertain whether our copper-zinc couple was capable of effecting the decomposition of amyl iodide with production of an organo-metallic body.

On performing the experiment in a manner analogous to that described in our previous communication on iodide of ethyl, we at once perceived that it was a question of temperature. At 100° there is no appreciable action, but upon heating the flask somewhat higher in a paraffin bath, decomposition ensues. It however, proceeds slowly, unless the temperature be raised to near the boiling-point of the iodide (146°); but at such a temperature 5 c.c. of amyl iodide are completely converted in about a quarter of an hour. Volatile bodies are formed which, if allowed to distil over into a receiver, are found to have the properties of amyl hydride and amylene described above, while in the flask there remain another limpid liquid and a white crystalline body, which appears to be but sparingly soluble in it. If the flask be now heated a little higher, this liquid distils over, and on examination proves to consist almost wholly of one substance, having the properties of Frankland's amyl. At about the temperature necessary to distil off the amyl, there begins to form a body which fumes in the air; and at 160°, or above, the white crystals suffer decomposition, with production of a liquid that distils over, and leaves a solid substance in the flask. The liquid is again almost pure amyl.

As both stages of this reaction have yielded amyl, this would appear to be a productive method of preparing that substance. It was evidently worthless, however, for the preparation of zinc-amyl, unless it could be modified in some favourable direction. Such a modification was not far to seek. If during the formation of the crystalline body, the volatile hydrocarbons are caused to fall back again into the flask, and then the contents are rapidly distilled off either over a flame or by a bath at 160° or higher, a good deal of zinc-amyl is carried over with the other liquids, and collects with them in the receiver.

The following are the quantitative experiments that were performed, arranged according to the temperature at which the first operation was conducted. As in the case of the ethyl iodide 5 c.c. were always

employed, and the amount of zinc compound distilled was estimated by shaking the contents of the receiver with water, and weighing the oxide produced.

Experiment.	Temperature of bath.	Duration of heating.	Amount of decomposition.	ZnO obtained.	Zinc-amyl indicated.
A......	100°	1 hour	none	none	— grm.
B......	127°—131°	1 „	about 2 c.c.	0·095 grm.	·241 „
C......	127°—130°	3 hours	complete	0·324 „	·834 „
D......	138°—142°	2 „	„	0·222 „	·571 „
E......	140°—160°	2 „	„	0·150 „	·386 „
F......	145°	7·5 min	4·25 c.c.	0·320 „	824 „
G......	145°	15 „	complete	0·444 „	1·143 „
H......	145°	20 „	„	0·406 „	1·015 „
I......	177°—188°	1 hour	„	none	— „

As the amount of zinc-amyl theoretically attainable from 5 c.c. of the iodide is 3·97, the best of the above experiments gave only ·28 per cent. of what might have been hoped for.

It then occurred to us that if the zinc-amyl, which is said to boil at 220°, could be raised in vapour at or near the temperature at which the crystalline body splits up, that is about 150°, it might be procured in larger quantity. The first part of the operation was therefore performed as before, namely, by heating the flask in a paraffin bath at 145° for 15 or 18 minutes, but a pump was attached to the distilling apparatus, and a good vacuum was made. The flask was then heated, and the vapour was pumped into water.

The results were :—

Experiment.	Second heating.	ZnO obtained.	Zinc-amyl indicated.
J	By gas flame........	0·621	1·59
K	By paraffin bath	0·678	1·73

This shows a much larger yield of the zinc-amyl, in fact 40 and 43·5 per cent. of the theoretical quantity.

Of course in the receiver it is mixed with the hydrocarbons, especially the less volatile amyl. By careful heating, the great bulk of that liquid may be separated by distillation; but as we operated on small quantities and the zinc-compound is easily decomposed, we never obtained it in the pure state; still, it answered sufficiently to the description given by Frankland of the zinc-amyl he prepared by the action of mercuric-amyl on zinc, to leave no doubt that it was the same substance.

Frankland has pointed out the perfect analogy of the decomposi-

tion of amyl iodide into the liquid $C_{10}H_{22}$, C_5H_{12}, and C_5H_{10}, with the secondary reactions by which ethyl iodide yields the gaseous C_4H_{10}, C_2H_6 and C_2H_4. But working as he was obliged to do, with zinc-amalgam at a temperature above the boiling-point of amyl-iodide, he obtained little else than the secondary action which we find to accompany the formation of amyl-iodide of zinc through the agency of the couple at a lower temperature. We may extend the analogy, for just as the crystalline $C_2H_5I.Zn$ forms in the one case, so does the crystalline $C_5H_{11}I.Zn$ form in the other; two molecules of the one split up by heat into $C_4H_{10}Zn$ and ZnI_2, and two molecules of the other into $C_{10}H_{22}Zn$ and ZnI_2, while in each instance this splitting up is accompanied by a similar secondary reaction. In the case of the ethyl compound, however, this secondary reaction appears to be principally—

$$2C_2H_5IZn = ZnI_2 + Zn + C_2H_6 + C_2H_4.$$

while in the case of the higher carbon molecule, it is mainly—

$$2C_5H_{11}IZn = ZnI_2 + Zn + C_{10}H_{22}.$$

Action on Amyl Iodide and Water or Alcohol.

As zinc alone is capable of decomposing a mixture of amyl iodide and water at 140° with production of amyl hydride, it was interesting to ascertain whether our couple would do the same at a lower temperature.

The experiment was conducted as in the case of the ethyl-compound by pouring 5 c.c. of the iodide on to a couple washed with water but not dried. Action was found to take place slowly at the temperature of the laboratory 10°, but in a water-bath at 100° it proceeded so rapidly that it appeared complete in an hour and a-half. The vapours produced were made to pass up a tube about 16 inches long, which condensed any volatilised water or iodide, and then through a Liebig's condenser into an iced receiver. A liquid was thus collected which was lighter than water, not miscible with it, and boiled when the vessel containing it was immersed in a bath at 33°, a thermometer in its vapour registering 29°. Any further proof that this was the same hydrocarbon as Frankland obtained at a higher temperature, seemed unnecessary. The residue in the flask resembled that from the ethyl compound treated in the same manner.

We repeated this experiment, using absolute alcohol instead of water, and found as before that the action proceeded slowly at 10°, but at 70° it seemed to be complete in three-quarters of an hour. The same volatile hydrocarbon was produced; and the residue in the flask gave the properties of the iodo-ethylate of zinc described in our former

paper as occurring when ethyl iodide and alcohol react in presence of the couple.

This circumstance, and the fact that no permanent gas is given off during the experiment with the amyl compound, show that it is the radical of the iodide, and not that of the alcohol, which is hydrogenised.

This reaction offers a ready method of preparing pure amyl hydride.

Action on Methyl Iodide and Water or Alcohol.

Methyl iodide was found to be decomposed very slowly by a dry copper-zinc couple, even at the boiling-point of the liquid.

If, however, the couple be wet with water, decomposition proceeds even at the ordinary temperature. An experiment made as usual with 5 c.c. of the iodide at 12°, the flask being shaken from time to time, evolved permanent gas during 18 hours, at the end of which time 1414 c.c. had been evolved.

This gas, after being washed, burned with a blue scarcely luminous flame. It was passed through bulbs containing alcohol to remove any vapour of the iodide, and afterwards through water, and analysed by Bunsen's method. There was no absorption by fuming sulphuric acid.

After removal to the eudiometer, the following data were obtained:

	Vol. observed.	Temp.	Diff. of Hg. level.	Barometer.	Vol. at 0° C. and 1 m. pressure.
Gas used (moist)	35·944	10·2	451	745·72	10·027
After addition of air and O (moist)	216·369	10·3	249·5	751·56	117·210
After combustion (moist).....	217·27	9·0	277·9	750·3	97·339
After absorption of CO_2 (dry)	198·86	11·0	297·1	752·31	87·238

which gave the following numbers as compared with those calculated for methyl hydride:—

	Found.	Calculated.
Gas burnt	10·03	—
Contraction	19·87	20·06
Carbonic acid ..	10·10	10·03

The amount of this gas which might have been evolved, according to theory, from 5 c.c. of methyl iodide is 1782 c.c.

The residue in the flask was similar to that in the corresponding reaction with iodide of ethyl and water. The nature of the reaction is evidently the same, and may be thus expressed—

$$CH_3I + H_2O + Zn = CH_4 + Zn\begin{cases} I \\ HO. \end{cases}$$

When 10 c.c. of absolute alcohol were added to 5 c.c. of methyl iodide, and the mixture was submitted to the action of the couple at 10°, it was about 20 minutes before evolution of gas commenced, but then the temperature inside the flask rose, and the action proceeded so rapidly that in half an hour 500 c.c. were obtained. The total collected was 897 c.c. In another experiment, where the iodide was poured on to a couple wet with alcohol, and the flask was immersed in water at 12°, the gas amounted to 1063 c.c. It burnt with a blue scarcely luminous flame. The residue in the flask gave the reaction of the iodo-ethylate of zinc, as in the analogous experiments with ethyl and amyl-compounds.

Either of the reactions just described offers a simple method for preparing pure methyl hydride, or marsh-gas.

XXVIII.—COMMUNICATIONS FROM THE LABORATORY OF THE LONDON INSTITUTION.

No. XI.—*Action of the Acid Chlorides on Nitrates and Nitrites.* Part I. *Action of Acetic Chloride.*

By HENRY E. ARMSTRONG.

THE relation between the dicarboxylic acids of the benzene series—the three phthalic acids—and other di-derivatives of benzene, has of late frequently been the subject of discussion, and has led to much experimental investigation on the part of various chemists. The results which have been obtained are, however, in many cases somewhat contradictory, and it is especially desirable that we should seek for new modes of directly converting the acids in question into other di-derivatives of the same parent hydrocarbon, benzene.

The object in instituting the experiments which have resulted in the observations described in this preliminary notice was thus to seek for a method of converting phthalic acid, and if possible its isomerides also, into the corresponding dinitrobenzenes.

It is well known that a class of compounds has been obtained by Schützenberger from certain of the acids of the acetic and benzoic series, which are perhaps most appropriately termed *haloïd salts*, since they may be regarded as derived from the metallic salts of those acids by the replacement of the metal by the halogens. Thus, by the action of chlorous anhydride on acetic anhydride, Schützenberger obtained the compound, $C_2H_3ClO_2$, or acetate of chlorine—

$$\left.\begin{matrix}CH_3.CO\\CH_3.CO\end{matrix}\right\}O + \left.\begin{matrix}Cl\\Cl\end{matrix}\right\}O = CH_3.CO_2Cl + CH_3.CO_2Cl.$$

The corresponding bodies containing bromine and iodine (and cyanogen) were also examined by him. Characteristic of these compounds is their excessive instability: they break up readily into carbonic anhydride and the mono-haloïd derivative of the hydrocarbon, from which the acid yielding the haloïd salt may be regarded as primarily derived. For example, acetate of chlorine is resolved on heating into carbonic anhydride and chloromethane:—

$$CH_3.CO_2Cl = CO_2 + CH_3Cl.$$

It thus appeared probable that if a similar series of bodies derived from the acids, or rather from their metallic salts, by the replacement of the metal by the group (NO_3) could be obtained, these would be easily resolvable into carbonic anhydride and the nitro-derivative of a hydrocarbon. Compounds of this class might appropriately be termed *acid nitrates*. Such a series might be formed by the action of the acid chlorides on the metallic nitrates. Thus silver nitrate and acetic chloride would, it was thought, in the first place react as indicated by the equation:—

$$CH_3COCl + AgNO_3 = AgCl + CH_3.CO(NO_3).$$

As a matter of fact, however, the reaction takes a different and somewhat remarkable course. The addition of acetic chloride to silver nitrate is attended by the immediate evolution of gas, easily recognised as a mixture of nitric peroxide and chlorine, which continue to be liberated until for each molecule of nitrate employed two molecules of the chloride have been added. Much heat is evolved at the same time. At the conclusion of the experiment, after expelling the gases and any slight excess of acetic chloride by passing a current of dry air through the flask, which is heated to a temperature of about 100° in an oil-bath, there remains, together with a residue of silver chloride, a certain quantity of a liquid which may be distilled over at a somewhat higher temperature (below 140°), which is none other than acetic anhydride.

The reaction giving rise to the formation of these various products probably occurs at two stages, as represented by the equations—

$$(1.)\ C_2H_3OCl + AgNO_3 = C_2H_3AgO_2 + Cl + NO_2.$$

$$(2.)\ C_2H_3AgO_2 + C_2H_3OCl = \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O + AgCl.$$

It is possible, however, that the reaction presents only a single phase, and that the formation of the anhydride is immediate and not preceded by that of the acetate, as above represented, thus:—

$$\begin{matrix}C_2H_3OCl\\C_2H_3OCl\end{matrix} + AgNO_3 = AgCl + NO_2 + Cl + \left.\begin{matrix}C_2H_3O\\C_2H_3O\end{matrix}\right\}O.$$

A careful quantitative examination of the reaction, which it is proposed to execute, will doubtless enable a definite conclusion to be arrived at on this point.

It appears somewhat remarkable at first sight that free nitric peroxide and free chlorine should be obtained, and not the product of their union, the so-called *nitrylic chloride*, NO_2Cl. That they are uncombined, however, is proved, it is believed, by the fact that if the gas, as it is evolved, be passed through warm water, it loses its reddish-brown colour, the nitric peroxode being absorbed, and the unabsorbed gas which is then collected has the appearance of pure chlorine. Were the gas nitrylic chloride, we should expect to obtain nitric and hydrochloric acids and no chlorine on passing it into water.

Similar results have been obtained by substituting other nitrates for silver nitrate. Lead nitrate is at once acted upon, chlorine and nitric peroxide gases are evolved, and the residue consists of lead chloride and acetic anhydride.

Mercuric nitrate is also attacked immediately; much heat is evolved and gases are given off. This reaction, however, has not yet been examined.

Barium nitrate is not affected, but calcium nitrate is readily acted upon by acetic chloride.

Potassium nitrate is also at once attacked. It is remarkable that the gas at first evolved appears to consist almost wholly of chlorine, and it is not until the reaction has gone on for some time that nitric peroxide is also given off. The residue consists of potassium chloride and acetic anhydride.

Amylic nitrate is not acted upon by acetic chloride at the boiling point of the mixture.

Some preliminary experiments have also been made on the action of acetic chloride on nitrites. Gas is immediately evolved on the addition of the chloride to potassium nitrite; this gas resembles chlorine somewhat in appearance, but has a slight reddish-brown tinge, and is readily absorbed by water. Towards the close of the reaction, nitric oxide is also evolved.

On heating the flask to about 150° after the evolution of gas had ceased, a considerable quantity of acetic anhydride distilled over. In all probability the reaction takes place as represented by the equations:—

$$KNO_2 + CH_3.COCl = NOCl + CH_3.CO_2K.$$
$$CH_3.CO_2K + CH_3.COCl = \left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + KCl.$$

It is proposed to extend the above experiments and to examine carefully the behaviour of the acid chlorides in general, notably those derived from acetic, benzoic, succinic, sulphuric, and chromic acids on

the nitrates, in order to ascertain under what conditions nitric peroxide and chlorine are evolved, and under what other conditions nitrylic chloride* is obtained.

It may here be remarked moreover that several other methods are available which may, not without reason, be expected to yield the acid nitrates, the formation of which was discussed in the beginning of the communication.

These are :—

1. The action of nitrylic chloride on the metallic salts of the acids, *e.g.*—

$$C_2H_3O_2Ag + NO_2Cl = AgCl + C_2H_3O(NO_3).$$

2. The action of nitric anhydride on the acid anhydrides—

$$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + N_2O_5 = 2C_2H_3O(NO_3).$$

3. The action of nitrylic chloride on the acid anhydrides, which may perhaps give rise to the formation of the acid nitrate and acid chloride. Thus, in the case of acetic anhydride :—

$$\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O + NO_2Cl = C_2H_3O(NO_3) + C_2H_3OCl.$$

I hope shortly to be able to describe the result of experiments in these directions, upon which I am at present engaged.

XXIX.—*Isomeric Terpenes and their Derivatives.*—Part II.—*On Cymene from Various Sources.*

By C. R. A. WRIGHT, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

IN Part I it has been shown that the oil of nutmeg contains an isomeride of camphor, $C_{10}H_{16}O$ (first described by Gladstone, under the name of *myristicol*, and considered to be probably $C_{10}H_{14}O$); this substance is difficult to obtain pure, inasmuch as it occurs mixed with hydrocarbons of lower boiling-point and oxidised substances of higher boiling-point, from which it cannot be completely freed by fractional distillation, inasmuch as the myristicol itself alters by repeated distillation, becoming changed into polymeric modifications of higher boiling-point, and finally into a non-volatile resin.

* It has been shown by Prof. Williamson that chlorhydric sulphate and sodic nitrate yield nitrylic chloride.

§ 1. *Action of Phosphorus Pentachloride on Myristicol.*

When the purest myristicol that can be obtained (boiling at 212°—218°) is dropped on well-cooled phosphorus pentachloride, a vigorous reaction takes place, much hydrogen chloride and phosphorus oxychloride being formed; the complementary product is decomposed by distillation, and can therefore only be obtained approximately pure. In one experiment, where elevation of temperature during the reaction was avoided as much as possible, a yellowish-brown liquid was obtained, which gave the following numbers on analysis, after washing with cold water to remove hydrogen chloride and phosphorus oxychloride, and drying over calcium chloride:—

0·275 gram gave 0·717 CO_2 and 0·225 H_2O
0·311 „ „ 0·220 AgCl

Carbon	71·1
Hydrogen	9·1
Chlorine	17·5
Oxygen (by difference)	2·3
	100·0

No further action was exerted on this product by phosphorus oxychloride, whence it appears that the oxygen present was contained, not as myristicol, but as some other body not acted on by phosphorus pentachloride; on heating, much hydrogen chloride was given off, a hydrocarbon distilled between 170° and 190°, and a small quantity of a black resinous mass was left behind in the retort; this gave the following numbers, agreeing with the empirical formula $C_{10}H_{50}O_5$; it did not contain chlorine.

0·4355 gram gave 1·252 CO_2 and 0·328 H_2O

	Calculated for $C_{10}H_{50}O_5$.	Found.
Carbon	78·7	78·4
Hydrogen	8·2	8·4

Without doubt this resin contained the oxygen found as above in the chlorinated product, which, therefore, had the composition—

$$20C_{10}H_{15}Cl + C_{40}H_{50}O_5.$$

	Calculated.	Found.
Carbon	71·6	71·1
Hydrogen	8·7	9·1
Chlorine........	17·7	17·5

Hence the action of phosphorus pentachloride on the camphor-

isomeride forming the chief constituent of "myristicol," is expressed by the equation—

$$C_{10}H_{16}O + PCl_5 = HCl + POCl_3 + C_{10}H_{15}Cl.$$

which is perfectly parallel with the action of phosphorus pentachloride on alcohols generally.

$$X.OH + PCl_5 = HCl + POCl_3 + X.Cl.$$

The action of this reagent on camphor is, however, different (Gerhardt), being indicated by the equation

$$C_{10}H_{16}O + PCl_5 = POCl_3 + C_{10}H_{16}Cl_2,$$

whence it appears that camphor is a substance not belonging to the same series of compounds as myristicol, the former being apparently an aldehyde, $C_9H_{15}.CHO$, the latter an alcohol (probably a secondary one), $C_{10}H_{15}.OH$. Gerhardt and also Pfaundler have further shown (*Ann. Chem. Pharm.*, cxv, 29), that this dichlorinated camphor derivative splits up by heating into hydrogen chloride, and a body, $C_{10}H_{15}Cl$ (also obtainable by treating camphor with less phosphorus pentachloride than that required to form the dichlorinated body); this derivative is only isomeric with the body of same composition derived from myristicol, being, when pure, a crystalline body melting at 60°.

Louguinine and Lippmann have shown (*Bull. Soc. Chim. de Paris* [II], vii, 374), that when this crystalline body is heated for some length of time, or repeatedly distilled at a very slow rate, it splits up (like the chlorides of secondary alcohols) into hydrogen chloride and a hydrocarbon containing the elements of water less than the original camphor; thus—

$$C_{10}H_{15}Cl = HCl + C_{10}H_{14}.$$

The hydrocarbon thus produced appears to be ordinary cymene (*vide infra*, § 3); the isomeric chloride, $C_{10}H_{15}Cl$, produced from myristicol as just described, undergoes precisely the same reaction with even greater ease, one or two distillations of the crude chloride sufficing to yield a distillate, which (after distillation over sodium) has all the properties of cymene. The hydrocarbon thus obtained boiled between 174° and 179°, principally at 176°—178° (corrected). The numbers given on analysis and the investigation of its oxidation-products are given in §§ 9 and 11.

In one experiment where the myristicol employed was not wholly freed from lower-boiling terpenes, the action of phosphorus pentachloride gave rise to liquids which apparently were mixtures of the chloride, $C_{10}H_{15}Cl$, and polymerides of the terpene, $C_{10}H_{16}$, formed by the action of the hydrochloric acid set free during the reaction, or of

the phosphorus oxychloride thus produced; on distillation of the crude liquid, a resin, not volatile at 300°, was left in the retort; this gave—

Carbon	88·1	Hydrogen	11·3
„	88·2	„	11·3

indicating a mixture of $(C_{10}H_{16})_n$ and $(C_{10}H_{14})_n$, which would require carbon 88·9, hydrogen 11·1.

A polymeride, $(C_{10}H_{14})_n$, is described further on, obtained from camphor in an analogous way; Greville Williams also obtained a similar body (which he termed *paracymene*), together with ordinary cymene by the alternate action of bromine and sodium on caoutchene (*Jahresbericht*, 1860, 495).

§ 2. *Action of Zinc Chloride on Myristicol.*

The production of cymene from camphor by the action of dehydrating agents, such as zinc chloride or phosphoric anhydride, has been long known from the labours of Delalande, Gerhardt, and others; in the case of zinc chloride, however, Fittig, Kobrich, and Jilke have shown (*Ann. Chem. Pharm.*, 145, 129), that the action is by no means solely that indicated by the equation—

$$C_{10}H_{16}O = H_2O + C_{10}H_{14}.$$

A much more complicated decomposition also takes place, whereby a variety of other substances are produced simultaneously with cymene.

Myristicol was gently heated in a retort with about half its weight of solid zinc chloride; before the boiling-point was reached, an action was perceptible, and water distilled over; at 170° and upwards, a hydrocarbon passed over, and at 250° a yellow-brown non-volatile resin was left in the retort; this could readily be separated from zinc chloride by decantation and filtration while hot and semi-fluid; it gave the following numbers:—

0·331 gram gave 1·045 CO_2 and 0·313 H_2O.

	Calculated.		Found.
C_{20}......	240	83·91	83·58
H_{30}	30	10·49	10·51
O	16	5·60	—
$C_{20}H_{30}O$..	236	100·00	

The hydrocarbon which distilled was found (after treatment with sodium) to boil at 173°—177° (corrected); on analysis it appeared to be cymene; the numbers obtained and the results of its oxidation by chromic solution are given in §§ 9 and 11.

Hence the action of zinc chloride on myristicol is expressed by the reactions —

$$2C_{10}H_{16}O = H_2O + C_{20}H_{30}O = 2H_2O + 2C_{10}H_{14}.$$

The body $C_{20}H_{30}O$ is, perhaps, the ether of the alcohol $C_{10}H_{15}.OH$ (myristicol), viz., $\left.\begin{matrix}C_{10}H_{15}\\C_{16}H_{15}\end{matrix}\right\} O$; not impossibly, however, it may be a polymeride.

When the higher polymerides of myristicol are similarly treated, no cymene at all is formed; black resins result, one specimen of which contained carbon, 76·7; hydrogen, 8·2.

§ 3. *Cymene from Camphor by the action of Phosphorus Pentachloride.*

The experiments of Louguinine and Lippmann referred to above, were repeated in order to obtain another variety of cymene for comparison with the others; the product of the action of a slight excess of phosphorus pentachloride on camphor was heated in a flask with a long vertical tube attached as a condenser; for the first few hours hydrogen chloride was evolved; by-and-bye this ceased; the hydrocarbon was distilled off and digested in the same way with sodium; the body finally obtained appeared to be pure cymene, boiling at 175°—178° (corrected). Louguinine and Lippmann also found the boiling-point to be 175°—178°); its subsequent examination and analysis are given in §§ 9 and 11.

Simultaneously with this cymene, a polymeride of cymene appears to be formed in small quantity; a viscid tar not volatile at 300° was left in the retort after distilling off the cymene formed by the splitting up of the body $C_{10}H_{15}Cl$; this contained carbon, 89·05; hydrogen, 10·40; the formula $(C_{10}H_{14})_n$ requiring carbon, 89·55; hydrogen, 10·45.

§ 4. *Cymene from Nutmeg Hydrocarbon (precontained).*

It has been already stated in Part I that, by the action of sulphuric acid on the mixture of hydrocarbons boiling at 163°—164°, derived from oil of nutmegs by long-continued fractional distillation, the terpene present is polymerized and cymene is left unaltered; cymene thus obtained boiled at 173°—177° (corrected); its investigation and analysis are described in §§ 9 and 11.

§ 5. *Cymene from Oil of Turpentine (precontained).*

It has already been stated in Part I that ordinary oil of turpentine, when distilled over sodium, yields a hydrocarbon which is not (as usually supposed) a single body of formula, $C_{10}H_{16}$, inasmuch as

cymene can be isolated from it by the treatment with sulphuric acid previously referred to. The analysis and investigation of this variety of cymene are described in §§ 9 and 11. The hydrocarbon obtained boiled at 174°—177° (corrected), the hydrocarbon from which it was isolated boiling at 156°—159°; the quantity obtained was but small, about 3 per cent.

§ 6. *Cymene from Hesperidene Dibromide.*

Greville Williams showed (*Jahresbericht*, 1860, 495), that by the alternate action of bromine and sodium on caoutchene and turpentine, a hydrocarbon was formed apparently identical with cymene.

Barbier has recently found (*Bull. Soc. Chim. de Paris* [2], xvii, 18), that by treating terpin (the so-called hydrate of terebenthene) with bromine in the proportion of two equivalents or slightly more of the second to one of the first, water is eliminated and a dibrominated compound, $C_{10}H_{16}Br_2$, formed; when heated, especially in contact with caustic potash, this breaks up into hydrobromic acid and cymene, thus—

$$C_{10}H_{16}Br_2 = 2HBr + C_{10}H_{14}.$$

Oppenheim has since found that the same dibromide is formed by the direct union of two equivalents of bromine with the hydrocarbon of turpentine oil; heat alone causes the production of cymene only to a small extent, but heating in contact with aniline produces a large quantity of cymene (*Deut. Chem. Ges. Ber.*, v, 94 and 628). Citrene (from lemon oil) also unites with bromine, giving a dibromide which similarly splits up into hydrogen bromide and cymene.

In order to see if hesperidene would yield the same products, two equivalents of bromine were cautiously added through a capillary tube, to well-cooled hesperidene; no hydrobromic acid was evolved unless the temperature was allowed to rise considerably by too rapid addition. On heating the resulting slightly yellowish brown liquid, torrents of hydrogen bromide were evolved, and at 170° and upwards a liquid distilled, finally leaving behind an inconsiderable amount of a viscid brown resin; the distillate appeared to consist of a hydrocarbon and an unstable brominated compound, as hydrogen bromide was copiously evolved on redistilling the distillate after thorough washing with cold water and drying over calcium chloride. After three or four distillations, almost the whole of the hesperidene used was converted into cymene of considerable purity, the yield being, even in roughly conducted experiments, over 80 per cent. of the hesperidene employed. After boiling *per ascensum* with sodium for some time to destroy the last traces of brominated compounds, a hydrocarbon smelling exactly

like cymene and boiling at 175·5 to 177·5 (corrected) was obtained, only a few drops coming over below and above these limits respectively.

The analysis and investigation of this cymene are given in §§ 9 and 11; as this cymene is identical with all the other known forms of that hydrocarbon, it is evident that the dibromide of hesperidene undergoes precisely the same kind of reactions as the dibromides of citrene and the turpentine terpene, viz.:

$$C_{10}H_{16}Br_2 = 2HBr + C_{10}H_{14};$$

also that these three terpenes may all be regarded as *dihydrides of cymene.*

Not improbably the splitting up of the dibromide takes place in two stages, thus—

$$C_{10}H_{16}Br_2 = HBr + C_{10}H_{15}Br,$$
$$C_{10}H_{15}Br = HBr + C_{10}H_{14},$$

the unstable brominated compound above mentioned being the intermediate body, $C_{10}H_{15}Br$; it was, however, impossible to obtain any actual proof of this, inasmuch as analysis fails to detect whether the mixture obtained by the first distillation of dibromide is—

$$xC_{10}H_{14} + yC_{10}H_{16}Br_2,$$
$$\text{or} \quad (x-y)C_{10}H_{14} + 2yC_{10}H_{15}Br.$$

Cooling in a freezing mixture did not cause the separation of any solid body from the mixture.

Oppenheim states that by the action of chromic liquor on the dibromide of the turpentine terpene, bromine vapours are evolved, and terephthalic acid produced (not bromo-terephthalic acid as perhaps might be anticipated); by the action of chromic liquor on hesperidene dibromide, a resinous mass is produced which is only slowly attacked by the boiling chromic liquor, bromine vapours being evolved: by the complete oxidation of 50 grams of hesperidene dibromide, there were produced only a few decigrams of terephthalic acid, amounting to about $1\frac{1}{2}$ per cent. of the dibromide used: of this—

·0·4055 gave 0·852 CO_2 and 0·137 H_2O.

	Calculated.		Found.
C_8	96	57·83	57·30
H_6........	6	3·62	3·75
O_4........	64	38·55	—
$C_8H_6O_4$....	166	100·00	

It appears extremely probable that this small quantity was produced, not from the dibromide itself, but from a small quantity of cymene

present either formed by the splitting up of the dibromide by the heat evolved during its formation, or by the heat of the boiling chromic liquor; so that in all probability, hesperidene dibromide, like hesperidene itself, does not form terephthalic acid by oxidation: although, therefore, hesperidene is, like citrene and other terpenes, a dihydride of cymene, yet the relations of the hydrogen to the cymene are very different in hesperidene from what they are in the others, a circumstance that might perhaps be inferred from, and is certainly connected with, the difference in the amount of heat generated by the union of bromine with the terpenes (*vide* § 7), or by the action of sulphuric acid on these different isomeric bodies.

§ 7. *Cymene from the Dibromide of the Terpene of Nutmeg Oil.*

As has been shown in Part I, and in § 4 of this paper, the hydrocarbon boiling at 163°—164°, contained in oil of nutmeg, is a mixture of a terpene (dissimilar from the terpenes of turpentine, lemon oil, and orange oil) with ten or twelve per cent. of cymene. When it is treated with two equivalents of bromine, combination takes place between this terpene and the bromine, forming a dibromide very similar in characters to the dibromide of hesperidene, and like it, splitting up by the action of heat alone into hydrogen bromide and cymene.

Two differences, however, are noticeable; in the first place, a much smaller yield of cymene is obtainable in this way, only about 55 per cent. of the hydrocarbon used being converted into pure cymene, and of this some 10 or 12 per cent. is precontained; the remainder becomes changed into brown or black resinous substances; secondly, the union of a given weight of bromine with the nutmeg hydrocarbon evolves much more heat than is produced by the combination of the same quantity of bromine with hesperidene; it was not, however, found practicable to obtain any very accurate calorimetric determinations of the actual quantity of heat produced in each case.

Without doubt this circumstance, together with the similar result noticed in the case of the action of sulphuric acid on these two terpenes (p. 551 of this volume), is intimately connected with the difference in boiling-point of the two terpenes (163°—164° for the nutmeg terpene, 178° for hesperidene), and with the different chemical reactions undergone by them; *i.e.*, is intimately associated with the question of the nature of their isomerism. It would be of great interest to examine carefully the different amounts of heat generated by the combustion of equal weights of isomeric terpenes; but independantly of the difficulty in the way of obtaining sufficiently accurate results to be of any use in investigating the character of the differences between such isomerides, the previous experiments indicate that it is

not improbable that many bodies supposed to be pure terpenes may really be mixtures, and that in particular small percentages of cymene may be contained in them; the presence of this hydrocarbon would of course vitiate the results.

It may be predicted with considerable probability that the heat of combustion of hesperidene will be found to be less than that of the nutmeg terpene, a result quite in harmony with Julius Thomsen's results (*Deut. Chem. Ges. Ber.*, v, 769). Thomsen finds that in the case of analogous compounds, the higher the "molecular weight," the less is the heat of combination, thus—

$H_2 . O$	+ 68357	$H . Cl$	+ 22001
$H_2 . S$	+ 4512	$H . Br$	+ 8440
$H_2 . Se$	−	$H . I$	− 6036

As a rule, the higher the "molecular weight," the higher the boiling-point in comparable cases (*e.g.*, the well-known increase of boiling-point by about 20° for each additional CH_2 in truly homologous series), so that it appears not improbable that it may be a general rule that, *cœteris paribus*, the higher the boiling-point the less is the heat rendered sensible in the formation of a given compound, and therefore the greater is the "energy" of that compound.

It is well known that the greater the heat evolved in the formation of a compound, the more stable it is; thus metallic zinc decomposes water (as in the "couple" of Gladstone and Tribe), because more heat is evolved in the formation of ZnO than in that of H_2O; and for the same reason mercury displaces silver from its salts, copper precipitates mercury, and zinc copper, and so on. Hence it might be inferred that the compounds of hesperidene would probably be less stable than those of its isomerides of lower boiling-point, which seems to be the case at any rate with the dibromides, Oppenheim having found that the dibromide of turpentine (the hydrocarbon boiling at 160°—161°) is but little affected by heat, whilst as stated above the dibromide of hesperidene (b.-p. 178°) is readily split up into cymene and hydrogen bromide by simply heating it, the dibromide of the nutmeg hydrocarbon (b.-p. about 164°) having an intermediate stability.

The cymene obtained from the nutmeg dibromide boiled at 176°—178°; its analysis and the investigation of its oxidation products are given in §§ 9 and 11.

§ 8. *Cymene from Cummin Oil.*

Cummin oil was distilled whereby a distillate was obtained at 170°—250°, about 15 per cent. of a resin, not volatile at 300°, being left in the retort. This gave numbers agreeing with the empirical

formula, $C_{14}H_{17}O$, as it contains 83·35 p. c. carbon and 8·87 hydrogen. The distillate was agitated with a concentrated solution of sodium-hydrogen sulphite. whereby a thick magma of crystals was formed; this was pressed in folds of linen whereby the uncombined cymene was squeezed out, floating on the top of the liquors thus extracted. The cymene thus separated from the cuminic aldehyde also contained in the oil was treated with strong sulphuric acid, whereby much heat was evolved, the mixture becoming chestnut-coloured; water was added, and the viscid oil which floated to the top was removed and again subjected to the same treatment. On distillation part of the oily layer passed over at 175°—180°, the remainder constituting a viscid liquid resin not volatile at 300°. This contained 81·95 p. c. carbon, and 10·13 hydrogen, whence it appears that the resin was formed by the dehydrating action of the sulphuric acid on the cuminic aldehyde not completely separated by the treatment with sodium-hydrogen sulphide.

The volatile hydrocarbon was boiled with sodium for some hours, it then distilled at 175·5—177·5 (corrected), only a very few drops passing over below and above these limits respectively; the total quantity obtained was less than 20 per cent. of the oil used, that obtainable in a pure state being about 15 per cent. The analysis and oxidation products of this sample are given in §§ 9 and 11.

Of all the processes tried for preparing cymene, that described in § 6 (heating hesperidene dibromide) gave by far the best result as regards quantity and purity of product and ease of preparation.

§ 9. *Analyses of the foregoing Varieties of Cymene.*

A. From myristicol by action of phosphorus pentachloride—
0·2255 gram gave 0·738 CO_2 and 0·221 H_2O,
0·2250 gram gave 0·729 CO_2 and 0·220 H_2O.

B. From myristicol by zinc chloride—
0·269 gram gave 0·875 CO_2 and 0·271 H_2O.

C. From camphor by phosphorus pentachloride—
0·2265 gram gave 0·7445 CO_2 and 0·220 H_2O.

D. Pre-contained in nutmeg hydrocarbon distilling at 163°—164°—
0·3010 gram gave 0·9825 CO_2 and 0·295 H_2O.

E. Pre-contained in oil of turpentine—
0·2070 gram gave 0·675 CO_2 and 0·209 H_2O.

F. From hesperidene dibromide—
0·2625 gram gave 0·8595 CO_2 and 0·2540 H_2O.

G. From nutmeg terpene dibromide—
0·2515 gram gave 0·820 CO_2 and 0·244 H_2O.

H. Contained in cummin oil—

0·2500 gram gave 0·818 CO_2 and 0·243 H_2O,
0·2010 gram gave 0·656 CO_2 and 0·196 H_2O.

	Calculated.		Found.									
			A.		B.	C.	D.	E.	F.	G.	H.	
C_{10} ...	120	89·55	89·26	88·36	88·70	89·62	89·02	88·93	89·31	88·92	89·24	89·01
H_{14} ..	14	10·45	10·88	10·86	11·19	10·79	10·89	11·22	10·75	10·79	10·80	10·80
$C_{10}H_{14}$	134	100 00										

§ 10. *Boiling Points of the foregoing varieties of Cymene (corrected).*

A.	B.	C.	D.	E.	F.	G.	H.
176–178	173–177	175–178	173–177	174–177	175·5–177·5	176–178	175·5–177·5

Noad found 171·5°; Gerhardt and Cahours 175°; Church 171° before treatment with sulphuric acid and 175°—176° after, and Warren 179·5° for cymene from cummin oil; whilst cymene from camphor by zinc chloride was found to boil at 173°—176° by Fittig Köbrich and Jilke, and is stated to boil at 177°—179° (Kekulé, *Lehrbuch*); that from phosphoric anhydride and camphor was found by Delalande to boil at 175°. Oppenheim fround the cymene produced from the dibromides of citrene and terebenthene boiled between 176° and 179°; whilst Louguinine and Lippmann found the cymene obtained from the product of the action of phosphorous pentachloride on camphor boiled at 175°—178°.

§ 11. *Action of Chromic Liquor on the foregoing varieties of Cymene.*

All the above-described specimens of cymene were oxidised by a large excess of a mixture of 2 parts potassium dichromate, 3 sulphuric acid, and a bulk of water equal to that of the sulphuric acid; an inverted condenser being attached, boiling was continued until the liquid which dropped back appeared no longer oily, *i.e.*, until nothing but slightly acid water distilled; this required about 30 or 40 consecutive hours' boiling for quantities of 8 to 20 grams of cymene.

In every case terephthalic acid was produced; the acid was purified by solution in ammonia and precipitation by hydrochloric acid, and careful search was made in each case for isophthalic acid, but without success; the acid dissolved out by boiling water or alcohol and that obtained by boiling the barium salt with water and precipitating the dissolved part by acids, appearing in every case to be pure unaltered terephthalic acid. In several cases the resulting acid was analysed; when this was not done, the peculiar physical properties of terephthalic acid were carefully noticed. The following numbers were obtained:—

A. From myristicol by pentachloride of phosphorus: terephthalic acid obtained = 40 per cent. of cymene used—

0·4020 gram gave 0·845 CO_2 and 0·138 H_2O.

B. From camphor by pentachloride of phosphorus, about 35 per cent.—

0·2895 gram gave 0·617 CO_2 and 0·103 H_2O.

C. From turpentine oil by sulphuric acid, about 30 per cent.—

0·3775 gram gave 0·797 CO_2 and 0·135 H_2O.

D. From hesperidene dibromide, nearly 45 per cent.—

0·414 gram gave 0·878 CO_2 and 0·140 H_2O.

E. From dibromide of nutmeg hydrocarbon, about 25 per cent.—

0·3755 gram gave 0·801 CO_2 and 0·1345 H_2O.

F. From cummin oil, about 60 per cent.—

0·4000 gram gave 0·842 CO_2 and 0·137 H_2O.

Calculated.			Found.					
			A.	B.	C.	D.	E.	F.
C_8	96	57·83	57·32	58·12	57·59	57·84	58·17	57·41
H_6	6	3·62	3·81	3·94	3 97	3·76	3·98	3·80
O_4	64	38·55						
$C_8H_6O_4$ ..	166	100·00						

Hofmann found (*Ann. Chem. Pharm.*, xcvii, 197) that cymene from cummin oil yielded by oxidation with chromic acid an acid which had the characters of terephthalic acid, but to which he attributed the formula $C_9H_8O_4$. De la Rue and Müller (*Ann. Chem. Pharm.*, 121, 88), and Schwanert (*Ann. Chem. Pharm.*, 132, 258), found that this so-called *insolinic* acid was only impure terephthalic acid.

Fittig and Ferber found that the cymene formed from camphor by zinc chloride did not yield terephthalic acid by oxidation (Kekulé, *Lehrbuch*, ii, 542); De la Rue and Müller, on the other hand, found (*loc. cit.*) that terephthalic acid was produced by oxidizing this variety of cymene. These contradictory results, together with those obtained by Riche and Bérard (*Jahresbericht*, 1864, 531) which led Kekulé (*Lehrbuch*, *loc. cit.*) to regard the cymene from cummin oil as different from that obtained from camphor, may no doubt be explained by the observations of Fittig, Köbrich, and Jilke that camphor yields a very complex mixture of products by the action of zinc chloride, and consequently that the cymene thus obtained is exceedingly impure.

The chromic liquors obtained in the above experiments were distilled and the distillate neutralized by soda and evaporated to a small bulk; a quantity of sulphuric acid, insufficient to neutralize the whole of the sodium present, was then added and the whole distilled, the distillates being converted into silver salt by treatment with silver carbonate. Had any higher homologues of acetic acid been present they must have been contained in the distillate; no appreciable quantity, however, appeared to be present in any case. After drying over sulphuric acid in the dark, and finally at 100°, the silver salts gave these numbers, agreeing in each case with those required for acetate;—

A. From myristicol by pentachloride of phosphorus—
0·795 gram gave 0·511 metallic silver.

B. From camphor by pentachloride of phosphorus—
0·2025 gram gave 0·1315 Ag.

C. From turpentine oil by sulphuric acid—
0·428 gave 0·278 Ag.

D. From hesperidene dibromide—
1st specimen, 0·3935 gave 0·2540 Ag.
2nd specimen, 0·509 gave 0·3285 Ag.

E. From dibromide of nutmeg terpene—
0·623 gave 0·4005 Ag.

F. From oil of cummin—
0·430 gave 0·278 Ag.

Calculated.			Found.						
			A.	B.	C.	D.		E.	F.
$C_2H_3O_2$ ..	59	35·32							
Ag......	108	64·68	64·27	64·92	64·95	64·52	64·54	64·29	64·65
$C_2H_3AgO_2$	167	100·00							

In the other cases, where an analysis was not made, the qualitative reactions of acetic acid were obtained.

Oppenheim has found terephthalic and acetic acids to be formed by the oxidation of the cymene from turpentine dibromide and that from citrene dibromide; but he also observed the formation of small quantities of camphor formed by the reaction—

$$C_{10}H_{14} + H_2O = C_{10}H_{16}O.$$

This substance was carefully looked for in each of the above cases, but was not found in any one instance.

§ 12. *Physical Properties of the foregoing Varieties of Cymene.*

In odour the eight varieties of cymene described above were indistinguishable one from another.

Dr. Gladstone has kindly determined the specific gravities, refractive indices, and dispersive powers of the above-described specimens of cymene, and finds that the differences are in no case greater than those usually noticed in different preparations of the same substance, such differences being due to error of observation and adhering traces of impurity. In all cases the numbers obtained approximate closely to the following mean values:—

Specific gravity	0·86
Refractive index	1·48
Dispersion	0·035

§ 13. *Conclusions.*

The foregoing results, summed up in §§ 9 to 12, indicate that there is but one variety of cymene produced from and existing in the bodies experimented with; this boils at 176° to 177°, and yields by oxidation terephthalic acid (in quantities much less than those theoretically obtainable) free from isophthalic acid; acetic acid free from higher homologues is also produced.

The production of terephthalic acid from cymene by oxidation shows that *two* "lateral chains" are present; and as toluic acid is also obtainable from cymene, one of these chains must be methyl (since toluic acid gives rise to methyl-benzene = toluene). Cymene therefore is either a methyl-propyl-benzene or a methyl-isopropyl-benzene.

If terephthalic acid be regarded as a 1 : 4 benzene derivative, there are but three formulæ attributable to bodies which can form cymene by loss of H_2, viz.:—

$$C_6(PrH) . H_2 . H . Me . H . H.$$
$$C_6Pr . H_2 . H_2 . Me . H . H.$$
$$C_6Pr . H . H_2 . (MeH) . H . H.$$

(where it is not stated whether Pr = ordinary propyl or isopropyl).

Four bodies are, however, now known which are apparently homogeneous and different substances, and yielding the same cymene by removal of H_2, viz.:—

The terpene of turpentine oil } Williams, Barbier,
" " lemon " = citrene } Oppenheim.
The terpene of orange oil = hesperidene } Wright.
" " nutmeg " } Wright.

Hence it must be supposed either that terephthalic acid is not a 1 : 4 dicarboxyl-benzene, or else that one at least of these hydrocarbons is really the dihydride not of a 1 : 4, but of a 1 : 3 or a 1 : 2 methyl-propyl-benzene, the radicals methyl and propyl altering their mutual relations to one another during the elimination of the H_2, and finally arriving at the 1 : 4 position.

Whatever may be the actual character of the process thus symbolically indicated, there can be little doubt that it corresponds to the performance of "internal work" of some kind, and therefore that a change of this kind is probably coincident with the evolution of a quantity of heat less than that which would be produced by the removal of H_2 from the hydride of a 1 : 4 compound; if, therefore, it were possible to estimate the quantity of heat involved in the reactions—

$$C_{10}H_{16} + Br_2 = C_{10}H_{16}Br_2,$$
$$C_{10}H_{16}Br_2 = 2HBr + C_{10}H_{14},$$

some light might be thrown on the subject of the "structural" formula of the terpenes; unfortunately such determinations appear to be impracticable.

If terephthalic acid be viewed as a 1 : 3 benzene derivative, 6 formulæ exist indicating the dihydrides of cymene, and if as a 1 : 2 derivative, there will be 6 other formulæ, viz.:—

$$1\,.\,3\left\{\begin{array}{llllll}
C_6\,.\,(PrH) & .\,H_2 & .\,Me & .\,H & .\,H & .\,H. \\
C_6\,.\,Pr & .\,H_2 & .\,(MeH) & .\,H & .\,H & .\,H. \\
C_6\,.\,Pr & .\,H & .\,(MeH) & .\,H_2 & .\,H & .\,H. \\
C_6\,.\,Pr & .\,H & .\,Me & .\,H_2 & .\,H_2 & .\,H. \\
C_6\,.\,Pr & .\,H & .\,Me & .\,H & .\,H_2 & .\,H_2. \\
C_6\,.\,(PrH) & .\,H & .\,Me & .\,H & .\,H & .\,H_2.
\end{array}\right.$$

$$1\,.\,2\left\{\begin{array}{lllllll}
C_6\,.\,(PrH) & .\,(MeH) & .\,H & .\,H & .\,H & .\,H. \\
C_6\,.\,Pr & .\,(MeH) & .\,H_2 & .\,H & .\,H & .\,H. \\
C_6\,.\,Pr & .\,Me & .\,H_2 & .\,H_2 & .\,H & .\,H. \\
C_6\,.\,Pr & .\,Me & .\,H & .\,H_2 & .\,H_2 & .\,H \\
C_6\,.\,Pr & .\,Me & .\,H & .\,H & H_2 & .\,H. \\
C_6\,.\,(PrH) & .\,Me & H & H & H & H_2
\end{array}\right.$$

So that if it be supposed that the methyl and propyl groups can alter their mutual connections during the removal of H_2, there are altogether 15 different possible formulæ for dihydrides of cymene.

Postscript.—While this paper was being written, Riban communicated to the Chemical Society of Paris a paper (reported by Henninger in the *Berichte* of the Berlin Chemical Society, 1873, p. 199), wherein he states that he has obtained cymene from turpentine oil by treating it with sulphuric acid. Riban, however, appears to consider

that the cymene is produced by the removal of H_2 from $C_{10}H_{16}$, the sulphuric acid being simultaneously reduced to sulphurous acid. The writer, however, considers that the cymene is *precontained as such* for the following reasons.

1st. The analytical numbers obtained (Part I) with the hydrocarbon boiling at 163°—164° from nutmeg oil showed that there might be present a certain quantity of cymene without its presence being detectable by ordinary combustion; whilst the fractions boiling at 175°—177°, 177°—179° certainly contained cymene, which would render it next to impossible that a fraction boiling at only 10 or 12 degrees lower should be wholly free from that constituent. Hence the cymene obtained from the 163°—164° distillate was almost certainly precontained. If nutmeg oil contain cymene ready formed in addition to terpenes, the latter being in great excess, the same might be the case with other analogous bodies, *e g.*, turpentine.

2nd. Both nutmeg oil and turpentine yield terephthalic acid by oxidation, whilst hesperidene does not give a trace of that substance. By subjecting hesperidene to the treatment with sulphuric acid above described, no trace of cymene is obtainable, whilst both the other oils yield cymene by this process: hence it is highly probable that the terephthalic acid is derived in these instances (and in other analogous ones) from cymene precontained in the oils, and not from the terpene present. The possibility of hesperidene having a constitution of a kind utterly dissimilar from those of the nutmeg and turpentine terpenes, is negatived by the experiments described above, whereby it is shown that hesperidene and the nutmeg terpene are (like citrene and the turpentine terpene according to Oppenheim) *dihydrides of the same cymene.*

3rd. The production of sulphurous acid, which undoubtedly takes place when terpenes are mixed with strong sulphuric acid, not improbably arises from the further action of the acid on the terpene polymeride formed; and although it is conceivable that this action might generate cymene, yet the production of this substance in this way is improbable, inasmuch as the action seems one of entire destruction, dark brown and black humus-like substances being formed. Hesperidene thus treated, yields much black humus-like substance, together with a large amount of sulphurous acid, but no trace of cymene. When the mixture of acid and terpene is kept cool, and the terpene added slowly, the formation of sulphurous acid and of black humus-like products, is much less than when the mixture is allowed to heat; by very cautiously working, the writer has succeeded in isolating cymene from oil of turpentine without the formation of more than inconsiderable quantities of sulphurous acid.

XXX.—*Note on Pyrogallate of Lead, and on Lead Salts.*

By W. H. Deering.

The only pyrogallates that appear to have been analysed, are the antimony compound of Rosing, and the lead salts. Of three lead salts, two described by Berzelius are obtained from solutions containing ammonia, and therefore would be difficult to obtain of definite composition. The third was prepared and analysed many years since by Dr. Stenhouse (*Gmelin's Handbook*, vol. xi, pp. 401, 402). With the view of controlling the formula given to it ($3PbO.4C_6H_6O_3$ by Dr. Stenhouse, or $2C_{12}H_{10}PbO_6.PbH_2O_2$* in Watts's Dictionary), the substance was re-examined.

The pyrogallic acid used was purified by crystallisation from boiling benzene, in which it is moderately soluble, and but slightly soluble in cold benzene. Traces of benzene can be removed from the crystals by shaking them up with cold bisulphide of carbon and then exposing them to the air.

The pyrogallic acid was dissolved in water, the solution acidulated with acetic acid, and precipitated by neutral acetate of lead in two portions: "A," while the liquid contained excess of pyrogallic acid; "B," by adding the acetate of lead in excess. The precipitates were washed several times by stirring up with cold water, and decanting, and were finally filtered and dried over sulphuric acid as described by Dr. Stenhouse. The moist salt oxidises somewhat quickly, but the dry salt oxidises but slowly.

Dried at 120° in a current of dry hydrogen, the salt had the following composition:—

	A.	
	I.	II.
C....	24·00	24·13
H ..	2·08	2·13
Pb ..	53·60	53·54
O....	20·32	20·20

B.		
Pb	1..	52·84 per cent.
	2..	53·24 „

The salt is decomposed slightly during the drying process, but the above numbers agree pretty well with the analysis of Dr. Stenhouse.

The substance is, however, a combination of pyrogallate and acetate of lead having the same percentage composition as $3PbO.4C_6H_6O_3$.

* There printed as $C_{12}H_{10}PbO_6.PbH_2O_2$; it should be $2C_{12}H_{10}PbO_6.PbH_2O_2.H_2O$, to agree with Dr. Stenhouse's percentage numbers.

	Stenhouse.	$3PbO.4C_6H_6O_3$.	$C_{12}H_{10}PbO_6.(C_2H_3O_2)_2Pb$.
C....	24·51	24·55	24·55
H ..	2·28	2·05	2·05
Pb ..	53·09	52·94	52·94
O ..	20·12	20·46	20·46

Preparations A and B gave acetic ether when gently warmed with alcohol and sulphuric acid. The acetic acid in A was estimated by decomposing the dried substance with dilute sulphuric acid, filtering from sulphate of lead, and distilling until charring took place and sulphuric acid began to distil over. The distillate was neutralised with precipitated carbonate of barium, the filtered liquid evaporated on the water-bath, during which operation any sulphite of barium is oxidised to sulphate, the liquid again filtered, evaporated, and the salt dried at 120° C.

"A" gave 32·3 per cent. $Ba(C_2H_3O_2)_2$ containing 53·2 per cent. Ba. (In a test experiment with pure acetate of lead, in which about the same quantity of carbonate of barium was used, the acetate of barium obtained contained only 53·2 per cent. Ba, the deficiency being probably owing to traces of impurities in the $BaCO_3$).

$C_{12}H_{10}PbO_6,(C_2H_3O_2)_2Pb$ corresponds to 32·6 per cent. $Ba(C_2H_3O_2)_2$, and barium acetate contains 53·7 per cent. Ba.

To show that the acetic acid was not derived from the splitting up of pyrogallic acid by the sulphuric acid, 0·5 gram pyrogallic acid was distilled to charring with dilute sulphuric acid, the distillate treated as above gave 0·006 gram $BaSO_4$ = about 0·3 part $Ba(C_2H_3O_2)_2$ per 100 of lead salt.

The above observation acquires importance from the fact that not a few insoluble lead salts of organic acids, in whose preparation acetate of lead is used, are said to consist of m molecules of lead salt + nPbO. It is possible that some of them may really be double salts containing acetate of lead.

XXXI.—*On Zirconia.*

By J. B. Hannay.

The properties of zirconium salts as prepared from various sources have been made the study of several chemists, the peculiarities observed in zirconia as usually prepared, leading some chemists to suppose that it consists of more than one oxide. The latest work of importance done in this direction was by Mr. H. C. Sorby, who in 1869 discovered some new absorption lines given by zircons when fused in a blowpipe

bead with boracic acid, and as these lines did not belong to any known element, he was quite justified in concluding the presence of a new substance. At his request, Mr. D. Forbes examined a specimen of zircon, and from his examination, he seemed to have separated a substance differing materially from zirconia, but as the amount of substance which he had to work upon was small, the examination was necessarily very incomplete. Mr. Sorby, in continuing his researches on the absorption spectrum of the supposed new substance, made the remarkable discovery that the two elements uranium and zirconium, when fused in a bead together, give an absorption spectrum differing materially from the spectrum of either taken singly, or what would have been expected to be produced by a mixture of the two. On examining this spectrum, he found that the combination of lines caused by the two elements agreed exactly with that which he had formerly ascribed to a new element.

The part which the spectroscope had played was thus accounted for, but the work which Mr. Forbes had done, as well as that by which former experimenters had been led to the supposition of the existence of another element, was still unexplained. For instance, Mr. Sorby had shown that the new absorption spectrum was caused by the minute traces of the other metals, but Mr. Forbes, in his experiments, obtained as much as 10 per cent. of the supposed new element. Now this amount of substance could not be said to be either uranium or cerium, as it is well known that these elements when present in zircons exist only in extremely small quantities.

Having lately come into possession of several specimens of zircon, I determined to submit the zirconia obtained from each to examination, with the view of setting at rest the disputed point as to the existence of this new metal allied with zirconia, supposed to exist in these gems, and more especially to examine the process used by Mr. Forbes in his analysis. I had three distinct varieties of zircon, the first consisting of reddish-grey very well crystallised nodules about the size of a pea, which weighed on the average 9 decigrams. The specific gravity of this variety was low, being from 4·01 to 4·29. The second consisted of very light grey crystals, very hard, and perhaps a little better crystallised than the first variety. The specific gravity of this sample was from 4·41 to 4·65. The third variety, of which I had only one specimen, consisted of a transparent, nearly colourless gem. It was extremely hard, and of specific gravity 4·725. The zircons were finely pulverized and fused with addition of a little pure soda, and when any remained undecomposed this was collected and fused again. Mr. Forbes separates the metals by treating the chlorides with hydrochloric acid, and the acid he directs to be used is of specific gravity 1·138. Now, this is a very dilute acid for such a purpose; indeed, it scarcely emits any

fumes. I, therefore, took three portions of the same sample. The first, after fusion and separation of the silica, was treated with acid of specific gravity 1·138, as used by Mr. Forbes; the second with acid of specific gravity 1·172; and the third with a strong acid of specific gravity 1·191. Whenever all the yellow colour was dissolved away, the treatment was stopped, and the pure zirconia precipitated by ammonia. The hydrochloric acid solution was treated in every case exactly as directed by Mr. Forbes, that is, precipitated by ammonia, and the hydrates so obtained were treated with tartaric acid, when the supposed new earth is left insoluble. Now, it is well known that hydrates like zirconia, when precipitated hot, are less soluble than when the precipitation takes place in a cold solution. The three portions above mentioned were therefore treated as follows. No. 1 was precipitated in an ice-cold solution; No. 2 in a solution at about 80°; while No. 3 was precipitated at the ordinary temperature, about 15°. The precipitates were treated in exactly the same way, that is, filtered and washed till quite pure; they were then treated with a large excess of tartaric acid, and kept at a temperature of 80° for about half an hour, when they were finally boiled and filtered. I may mention that the process of filtering off the insoluble residue was in some cases extremely tedious, and although conducted by means of a filter-pump, which kept up a vacuum of 650 mm., the filtration sometimes took fully 60 hours. The insoluble matter on the filter was dried, ignited, and weighed. The filtrate was treated with ammonia and ammonium sulphide to precipitate the iron, and after being allowed to stand several days the precipitate was filtered off, and the filtrate evaporated to dryness and ignited. When all the carbon from the decomposition of the tartaric acid was burned away and the earth left white, it was allowed to cool, and weighed. The following are the results of the analyses made on the same substance, but precipitated at different temperatures:—

	No. 1.	No. 2.	No. 3.
Silica	34·93	35·34	34·87
Zirconia	38·38	37·97	47·38
Supposed new earth	4·02	19·25	7·62
Supposed mixture of earths	22·01	6·84	9·27
Ferric oxide	0·51	0·54	0·53
	99·85	99·94	99·67

The difference caused by the variations in the concentration of the acid and in the temperature of precipitation are at once apparent on examining the above numbers, as the analyses were made with three portions of the same substance. In No. 1, which was treated with dilute acid, and might therefore have been expected to dissolve

more abundantly, I obtain only 4 per cent., because the hydrates were precipitated very cold, and so were very soluble in the tartaric acid; but I obtain 22 per cent. (soluble in tartaric acid) of what Mr. Forbes concluded to be a mixture of zirconia with the new earth. In No. 2 I obtain 19 per cent. of the new earth, because the zirconia was precipitated hot, and so rendered far less soluble in tartaric acid. The concentration of the acid in No. 3 caused it to dissolve far less of the zirconium chloride, and so I obtain 47 per cent. of pure zirconia, or about 10 per cent. more than with the dilute acid. That the soluble and insoluble modifications of zirconia are identical and not different earths will be seen from the following experiments. A solution of zirconium chloride was divided into two portions, one of which was cooled in a tube to nearly 0° C., and ammonia added until all the zirconia was precipitated. Tartaric acid was then added to the tube, and the contents of the tube were shaken and then boiled, whereupon the zirconia entirely dissolved. The other portion of the solution was heated to the boiling point and ammonia added, and again boiled for five or ten minutes. On addition of tartaric acid the zirconia refused to dissolve, and after boiling with strong solution of tartaric acid for five minutes, about four-fifths of the zirconia remained insoluble. When the zirconia solution is raised to the boiling point before the addition of the ammonia, the hydrate so obtained is frequently insoluble even in hydrochloric acid.

If the zirconia which is left insoluble in tartaric acid (which Mr. Forbes considered to be a new earth) be dissolved in sulphuric acid and the excess of acid expelled by heat, a sulphate is obtained which, when dissolved in cold water and precipitated by ammonia near 0° C., yields a hydrate easily soluble in tartaric acid, or at least soluble on boiling; so that, if the difference between zirconia and the new earth consists in the insolubility of the latter in tartaric acid, this experiment causes the difference to disappear entirely. Time is also an important element. For instance, I have seen a hydrate little affected after ten minutes, which was entirely dissolved after six hours' boiling with tartaric acid.

The great differences noticed in the deportment of the zirconium salts may be attributed in very many cases to the difference in treatment. I have found, however, that zircons of a high specific gravity yield a zirconia whose oxalate is generally insoluble or difficultly soluble in oxalic acid, whereas zircons of low specific gravity give an oxalate easily soluble in excess of acid. This may be owing to a difference in the conditions under which the zircons were formed in the rocks where they are found, or it may be due to the circumstance that zircons of low specific gravity usually contain other metals such as iron, etc.; in fact Mr. Sorby found that zircons of low specific gravity gave the

characteristic absorption spectrum showing the presence of uranium; whereas pure zircon of high specific gravity gave none.

When potassium or sodium silicofluoride is precipitated in a solution containing zirconia, a small quantity of the earth is always precipitated with the alkaline silicofluoride. The amount varies, and the earth so precipitated does not in any way differ from that which remains in solution.

When the earth which remains insoluble in tartaric acid is calcined it frequently gives an oxide which is extremely hard sometimes even harder than zircon, so that it retains a gritty feel after protracted grinding in an agate mortar. When this earth was dissolved in sulphuric acid, it gave a sulphate which answered all the usual reactions for zirconia, and when cooled to 0° and precipitated by ammonia yielded a hydrate quite soluble in tartaric acid. Both soluble and insoluble modifications yield the nearly insoluble precipitate with potassium sulphate.

I noticed some time since, when preparing specimens of the picrates of various metals, that two elements nearly alike in their inorganic salts, gave picrates entirely different in appearance. This is very noticeable in the picrates of barium and strontium, the former occurring in dull, brick-red, opaque prisms, whereas the strontium salt forms brilliant, golden-yellow, flat needles, which refract light strongly. I therefore thought that if the picrates of the soluble and insoluble modifications of zirconia were prepared, the appearance and composition of the salts might lead to some definite conclusion. I prepared the sulphates of the soluble and insoluble modifications, and added to their solutions an equivalent proportion of barium picrate. On filtering off the barium sulphate and evaporating the solution, I could obtain nothing but picric acid in solution, and on examining the precipitate I found it to consist of a mixture of barium sulphate and zirconia. I tried to effect the double decomposition at a temperature of 0° but on attempting to concentrate the solution, zirconia was precipitated, and picric acid alone remained in solution; I therefore abandoned the attempt to prepare zirconium picrate. I was equally unsuccessful in an attempt to prepare the zirconium salt of picramic acid.

Having finished my analytical work on the zircons, I determined to examine the absorption spectra, especially those of the impure specimens of low specific gravity. As my laboratory faces the north, I was unable to see or use sunlight, as Mr. Sorby did, and I have often found, when working with the spectroscope, that when an ordinary light is used, the violet end of the spectrum is very unsatisfactory, so before working on the spectrum of the zircons, I set about to find a light which would give a good violet. As I did not possess a battery of sufficient power to yield a steady electric light, I tried lime-light,

which gave a very good blue, but not so good as the brilliancy of the light would lead one to expect. The zirconia light, made by burning an oxyhydrogen jet against a cylinder of zirconia, gave a light extremely good in the violet, so that the slightest approach to a line could easily be detected, while the yellow was not more brilliant than when lime was used. The extreme red is also very distinct with this light. In front of the light I placed a screen with a lens in the centre, in whose focus I placed the bead for examination. By using a rather large lens, about 150 mm. in diameter, in conjunction with this light, a large dense bead may be brilliantly illuminated, and by using a thick bead, the lines are made very much more distinct. The use of the screen was of course to keep back all superfluous light, and in this case could not be dispensed with, as the zirconia light is so dazzling.

I prepared a bead of borax and added a little boracic acid, and then saturated this with zircon. The bead was raised to a bright red heat, and allowed to cool. As Mr. Sorby says, this clear, glassy bead gives no absorption bands. I wished to watch the formation of the lines, so I placed a foot blowpipe below the bead, so that the distance between the point of the flame and the bead was about 3 inches. I caused it to burn with a small blue flame, that the bead might be very gradually heated. Keeping my eye on the spectroscope, I placed the blowpipe exactly below the bead; at first no lines appeared, but after blowing a short time longer, a band suddenly shot across the violet end, and about five seconds after the other lines marked A, B, C, D, E and F made their appearance, at the same time the band in the violet split up into two lines, G and H, and a band I, with a nebulous edge. The band was not very distinct, and it was only with the powerful zirconia light that I observed it at all. Fig. 1 shows the spectrum seen at this period. I turned the blowpipe flame a very little up, and kept my eye on the spectrum at the same time. The two bands, G and H, in the violet became fainter, and then disappeared, but the nebulous band rather extended itself at first, then became faint, and when it disappeared the extreme end of the spectrum became dimmed with a kind of nebulous band, very indistinct, and without any edge. The two lines D and E in the green moved towards the violet end, F meanwhile becoming fainter, and finally disappearing, D broadened out into the line marked E in Fig. 2, B in Fig. 1 split up into the two lines C and D, while A narrowed down until it appeared as A in Fig. 2. C and F in Fig. 1 suddenly disappeared, while B appeared in Fig. 2. The whole change occupied only about three seconds. On applying a stronger heat, the lines grew fainter, when suddenly two nebulous bands appeared in the yellow; these disappeared immediately after, as suddenly as they had appeared. On applying further heat, the lines grew still fainter, and then all died out,

leaving a clear spectrum, the bead being glassy. I was so struck with these changes, especially as they differed slightly from the observations

FIG. 1.

FIG. 2.

of Mr. Sorby, that I examined minutely the mineral I had left. The powdered zircon was of specific gravity 4·01, and of a reddish-grey colour. As I wished, if possible, to detect any foreign metals, the following course was adopted in the analysis. The zircon was fused as usual, and the silica separated. The solution of the metals was then neutralized with ammonia and yellow sulphide of ammonium added, and when the precipitate had settled, the bulk of the liquid was decanted, and ammonium carbonate solution poured on the precipitate. This treatment should dissolve any uranium that the substance may contain, as the oxysulphide of uranium is soluble in ammonium carbonate. The solution was filtered and evaporated to dryness, then heated slightly to expel ammonium salts. As only a trace of residue remained, it was treated with two or three drops of aqua regia, the solution poured into a watch-glass, and after expelling the excess of acid, redissolved in water. On adding a drop of ammonia to this, a slight yellow precipitate soon became visible, but it was not weighable. On adding a drop of hydrochloric acid (to dissolve the precipitate), and then a drop of potassium ferrocyanide, a reddish-brown precipitate was plainly developed. These tests appeared to me to be quite conclusive of the presence of uranium.

The precipitate which remained insoluble in ammonium carbonate was dissolved in the smallest possible quantity of hydrochloric acid, and after the addition of tartaric acid, ammonia and ammonium sulphide were added. By this treatment, the iron is, of course, precipitated, while the other bases remain in solution. The solution containing the bases was evaporated to dryness and ignited to get rid of the tartaric acid. The oxide so obtained was dissolved in a small quantity of strong sulphuric acid, and the excess of acid expelled by heat. The sulphate was dissolved in water, and oxalic acid added in large excess. The precipitate at first formed seemed to dissolve entirely as the oxalate prepared from zircons of low specific gravity almost always does. On closer examination, however, there was seen to be a dimness through the liquid, and suspecting the presence of some foreign substance, I

allowed the beaker containing the solution to stand that the precipitate might subside. After standing for two days, the precipitate was seen to be entirely at the bottom of the beaker, and the supernatant liquid was perfectly clear. The solution was decanted as much as possible from the precipitate, which was collected on a very small filter and washed, then treated with strong nitric acid and dioxide of lead, when, after settling, the liquid had a distinctly yellow colour, characteristic of cerium. On examining the liquid with the spectroscope very carefully, I could distinguish the absorption-line of didymium in the yellow. I was unable to distinguish any others, but had the original amount of zircon been larger, I am sure they would have been easily seen. After concentrating the liquid, I applied special tests and confirmed the conclusion that both cerium and didymium were present. I thus find in the zircons, iron, uranium, cerium, and didymium, besides the silica and zirconia. Whether the cerium and didymium have anything to do with the curious changes observed in the spectrum I know not. The spectrum given agrees pretty well with that given by Mr. H. C. Sorby, except that the band marked F in Fig. 2 was not observed by him, and that the lines marked G H I were considered by him to be a single line; indeed, he did not discover it at all until he got exceptionally good sunlight. This shows the advantage obtained by using the zirconia light, and I would draw the attention of chemists and physicists to the great brilliancy it affords, especially in the violet end, thus giving a most searching light for spectroscopic work.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Spectral Lines of Low Temperature. By the Marquis of SALISBURY (Phil. Mag. [4], xlv, 241—245).

IF one secondary pole of a powerful induction-coil be connected with an insulated metal plate, the other pole being left unconnected, and a thermometer be fixed upright upon the plate, a green light will be visible in the vacuum above the mercury. This phenomenon, which in common with others of a like nature, would doubtless be explained by the somewhat vague term "induction," is considered in the present instance more especially worthy of notice, inasmuch as the exhibition of light is unattended with the slightest development of heat; whereas the heat produced by a discharge through an ordinary Geissler's tube is well known.

In a series of four experiments with a very delicate thermometer, a rise of three-quarters of a degree only was observed after five minutes, and this small expansion of mercury may even be attributed, and with great probability, to a secondary action.

Several lines are observable in the spectrum of this light, when the latter is examined with a spectroscope; with this peculiarity, however, that while thermometers constructed by the best makers give only three lines, instruments prepared by makers of less repute show at least four additional lines. Of these lines, the three former correspond to the brightest mercury lines, while the remainder coincide exactly with the strongest lines in tubes known to contain carbon compounds, and inasmuch as the wave-lengths of the latter were carefully verified, there is no reasonable doubt but that they are carbon lines.

The presence of these carbon lines is interpreted as a proof of slovenly preparation, the greasy film lining the interior of the thermometer not having been removed previous to the introduction of the mercury; and this appears to depend more upon the reputation of the maker than upon the price charged for the instrument, since a very cheap thermometer by a well-known maker showed only mercury lines, whereas a costly, but apparently very dirty thermometer by another maker, showed not only the four carbon lines, but one or two other faint green lines, the latter, however, too faintly to be identified.

The non-appearance of any hydrogen lines seems to be due to the fact that the specific luminosity of carbon, under electric excitement is much higher than that of hydrogen, or what amounts to the same expression, that hydrogen is non-luminous at a temperature at which carbon lines are distinctly visible: an explanation which was corroborated by direct experiment.

J. W.

Absorption of the Chemically Active Rays in the Sun's Atmosphere. By H. C. VOGEL (Phil. Mag. [4], xlv, 345—350).

THE observations of Secchi and Lias have shown that the light emitted by the sun is less at points near to the edges than at the more central points of the solar disc. The same has been shown by Secchi to be true of the sun's heat-rays. This, it appears, is due to absorption of light and heat by the atmosphere of the sun, the rays that proceed from the outer portion of the disc having to pass through a thicker layer of the surrounding atmosphere. The present author has sought to determine the diminution, due to the same cause, in the intensity of the chemical rays.

His experiments were made by means of photographs on paper sensitized with chloride of silver, taking advantage of the law of Bunsen and Roscoe, "*that equal products of the intensity of the light into the times of insolation correspond, within very wide limits, to equal shades of tints produced on chloride of silver paper of uniform sensitiveness.*" Thus, let I and I_1 represent two intensities, and t and t_1 the time of insolation, or exposure, if

$$I\,t = I_1\,t_1,$$

the shades of the exposed papers will be the same.

Having obtained photographs of the sun on sensitized paper, the author compared them from point to point with a scale prepared photographically, and obtained results, agreeing fairly, of which the following table may be taken as representative.

Calling the radius of the sun 12, and numbering from 1 to 12, so that the successive integers, E, shall represent the *apparent* distances of the various points from the centre, he obtains the corresponding intensities I:—

E	I.	E.	I.	E.	I.	E.	I.
0........	100	4	96·4	7	81·5	10	51·0
1........	100	5	93·7	8	77·0	11	33·0
2	99·4	6	89·8	9	66·0	12	13·5
3........	98·2						

The author has also made some experiments on comparative brightnesses, as far as chemical rays are concerned, of sun spots and of the penumbra.

The translator of the paper, A. Schuster, Esq., remarks that Prof. Roscoe had previously made experiments on the subject, which Vogel does not appear to have known. The results of the two investigators do not precisely agree. This may be due to the use of a refracting telescope. Vogel does not state whether this or a reflecting instrument was employed by him.

J. T. B.

On the Influence of Light of various Colours on the Spectrum of Chlorophyll. By J. CHAUTARD (Compt. rend., lxxvi, 1031—1033).

ALTHOUGH chlorophyll in alcoholic solution is rapidly altered by exposure to sunlight, it resists for a long time the action of light when dissolved in a fixed oil. The author has exposed solutions of chlorophyll to the action of light coloured by passing through variously-tinted solutions, and he states that the most luminous rays seemed to be the most energetic. Yellow light produced a modification in the spectrum more rapidly than red, and red light than blue.

W. A. T.

Production and mode of Action of the Silent Electric Discharge. By A. BOILLOT (Compt. rend., lxxvi, 628—630).

THE apparatus employed, by which ozone may readily be produced, consists of a closed glass tube filled with powdered animal charcoal, and having a platinum wire sealed into it. This is placed in the axis of two other concentric glass tubes, the space between these outer tubes being also filled with charcoal and furnished with a platinum wire. When these wires are attached to the terminals of an induction coil in action, the silent discharge passes between the two surfaces and oxygen is rapidly converted into ozone by its means. The vapour of sulphur in contact with oxygen was found to yield sulphurous acid accompanied by a little sulphuric acid; when the discharge passed, much sulphuric acid was produced. Again, hydrogen and the vapour of sulphur do not act upon one another, but with the discharge sulphydric acid is immediately formed.

C. E. G.

Researches on the Electricity of Plants. By JOHANNES RANKE (Ber. der. K. b. Akad., 1872, 177—199).

§§ 1 and 2. A current is always observed in a metallic connection between the uninjured surface and the cross-section of a plant. This current, already noticed by former observers, is termed the *false* current, because it does not circulate in the plant itself, but is produced by the chemical action of the liquids of the plant upon the metallic electrodes in contact with them.

§ 3. In order to obtain the *proper currents* of the plants, the following precautions were observed:—Pieces were cut out from the interior of the plant so that their whole surface was equally moistened with the liquid flowing out of it, and when the flow of the moisture was richer in one part than in another, the excess was removed by filtering-paper. As Sachs had shown that the liquids of the different tissues in most plants differ in their chemical reaction, the author chose for his first experiments *Rheum undulatum*, in the tissues of which no such difference can be observed.

It was also found necessary to use pieces with parallel fibres. The

apparatus employed were of the latest construction as devised by Dubois Reymond. A circular compensator was used, with one Daniell's cell and electrodes incapable of polarisation.

§ 4. *Fundamental Experiments on Leaf-stalks.*—*a. False Current.*—The cross-section of a piece obtained by two cuts at right angles to the longitudinal axis of the stalk was put in contact with one electrode whilst the uninjured epidermis was touched with the other. A current called the false current, is then found to flow in the connecting wire from the epidermis to the cross-section.

b. Proper Plant Current.—1. A piece is cut out from the leaf-stalk in the same way as described in *a*, but the epidermis is removed. If now connection be made as before, a current is found to flow in the connecting wire from the cross-section to the longitudinal section. This proper current of the plant corresponds with Dubois Reymond's strong current between cross-section and longitudinal section in muscles and nerves.

2. *The Weak Plant Current*—When on the cross-section or longitudinal section of a muscle or nerve, two points unsymmetrically situated with regard to the axis or to the equator are connected, Dubois Reymond's *feeble* currents are observed. Currents analogous, but flowing in the opposite direction, have been found to exist in vegetable tissues with parallel fibres.

3. *The Inclined Currents in Vegetable Tissues.*—Inclined currents analogous to those flowing from the obtuse to the acute corners of a rhombus which is cut out from a muscle, are observed in plants, but here they have the opposite direction.

4. *The electro-motive force of Plant Currents in Rheum* is about the same as in the nerve-currents.

5. The plant-currents vanish with the normal dying off of the plant-tissue. Living vegetable tissues have generally either an acid or a neutral reaction which turns alkaline when they die off in a moist atmosphere. The tissue may be considered as quite dead as soon as this change in the reaction is complete; *the normal currents then cease.*

§ 5. The existence of currents in other plants and other parts of the plant.

1. The currents observed in *Rheum undulatum* were found to exist in all other plants with parallel fibres. A long list of such plants is given.

2. Experiments on tissues with fibres not parallel:—

a. Roots of either cylindrical or not very marked conical shape show the true plant-currents; but those points of the longitudinal section from which the smaller roots branch off, behave like points of a cross-section.

b. Experiments on Pieces of the Stem.—Similar observations were made on the stem, or on pieces of the stem; on those points from which the vessels for leaves or twigs branch off.

3. The proper plant-current was also observed in some cases where the epidermis had not been removed. In general, however, the epidermis being a bad conductor seems to hinder the proper current from passing into the connecting-wire.

Conclusion.—The law of the plant-currents being established and proved to be analogous to that of the muscle and nerve-currents, we

may with some modifications apply Dubois Reymond's hypothesis of animal electricity to plants.

According to this hypothesis the interior of those parts of plants which are endowed with electro-motive force is filled with molecules embedded in a conducting substance and having their axes parallel to the axis of the part of the plant.

Whilst in animals the molecules are supposed to have two negative poles and a positive equator, it appears that *the molecules in plants have two positive poles and a negative equator.*

R. S.

On the Heat disengaged in the Reaction between the Hydracids and Water, and on the Molecular Volume of Solutions. By BERTHELOT (Compt. rend., lxxvi, 679—687; and Bull. Soc. Chim. [2], xix, 351—359).

THIS paper contains the author's results with hydrochloric acid, hydrobromic acid, and hydriodic acid, and the measure of the thermic formation of solutions of these hydracids of different degrees of concentration.

I. *Hydrochloric Acid.*—The author has found that an equivalent of the gas (36·5 grams) in the presence of 100 to 400 times its weight of water disengages + 17·43 heat-equivalents, and he also gives the thermic results obtained by the dilution of solutions of hydrochloric acid of different degrees of concentration, showing that the heat disengaged by dilution varies inversely as the quantity of water already united with the hydracid. The molecular volume of the solution $HCl + nH_2O_2$ is expressed by the formula—

$$V = 18n + \frac{10}{n}.$$

II. *Hydrobromic Acid.*—The heat evolved in this case by an equivalent of the gas, is + 20·7 heat-equivalents, and the effects of dilution are the same as those produced with hydrochloric acid, except that at the maximum of concentration the solutions of hydrobromic acid disengage somewhat more heat, a relation analagous to that obtained with the two gases. The molecular volume of the solution $HBr + nH_2O_2$ is expressed sensibly by the formula—

$$V = 18n + 25·5 + \frac{7}{n}.$$

III. *Hydriodic Acid.*—The author finds that $HI + 700\ H_2O_2$ disengages + 19·57 heat-equivalents, and that the heat disengaged on diluting the concentrated solution is nearly the same as that from hydrochloric acid and hydrobromic acid, from which it would appear that the molecular work accomplished in the reaction by these three hydracids on the same number of equivalents of water is the same. The formula representing the molecular volume of the solution $HI + nH_2O_2$ is—

$$V = 18n + 35·5.$$

At 0° C. one volume of water dissolves 500 volumes of hydrochloric acid gas, and at −12°, 560 volumes; of hydrobromic acid at 10°, about 600 volumes; and of hydriodic acid about 425 volumes.

An almost constant difference is observed between the molecular volumes of dilute solutions of hydriodic acid and hydrochloric acid, and also between hydrobromic acid and hydrochloric acid, which in the former case is 17·3 c.c., and in the latter 7·3 c.c. The same differences are found in dilute solutions of the chlorides, bromides, and iodides of potassium, sodium, and ammonium, also between the solid salts, the volume occupied by KI being 17·3 c.c. greater than that of KCl, and KBr 7·3 c.c. greater than KCl. Nearly the same differences in the molecular volumes exist in certain organic compounds, such as the chloride and iodide of acetyl. In numerous cases, however, this does not obtain, as in the comparison of the metallic salts; but it is always found that the molecular volume of a chloride is less than that of the bromide, and this again less than the corresponding iodide. This agrees with the thermic results obtained in the formation of these compounds, the formation of chlorides disengaging more heat than that of the bromides, which in their turn disengage more than the corresponding iodides. It would seem, moreover, that the formation of compounds which present an almost constant difference between their molecular volumes, corresponds with a nearly constant difference between the amount of heat disengaged.

C. E. G.

Industrial Production of Cold by the Expansion of Permanent Gases, and Air in particular. By J. ARMENGAUD (Compt. rend., lxxvi, 626—628).

IN air frigorific machines, the source of cold is obtained by means of air, which is first condensed, then cooled, and subsequently allowed to expand against a piston in such a manner as to exercise a certain exterior mechanical force which can be utilised in assisting to compress fresh quantities of air. The motive force required to work such a machine is the difference between the force expended in condensing the air, and that restored on its expansion. With regard to the manner of cooling the air which has become heated by compression, the author prefers to inject water into the cylinder of the pump during the compression; but, whatever method may be adopted, "the effective motive power required for the production of cold by the mechanical expansion of gases depends only, for a given mass, on the absolute initial temperature of the gas on entering the machine, and the degree chosen for the expansion." Moreover, the calorific power of the machine in respect of the motive power is independent of the nature of the gas. The motive power required when 2 is the degree of expansion and the cooling is performed during the compression of the gas, is only one-half of what it would be if cooled afterwards. As the motive power required increases with the degree of expansion, it is advisable to have this as low as possible compatibly with the intensity of cold which it is desired to attain: the number 2 is that which seems to be preferable. At this degree, and cooling the air during compression, one horse power, of 270,000 kilogram meters per hour, is theoretically capable of converting 41 kilograms of water at 20° into ice.

C. E. G.

On the Formation of the Sulphur Acids.

By JULIUS THOMSEN (Deut. Chem. Ges. Ber., v, 1014—1019).

1. THIS paper gives the results of a research on the affinities of the sulphur acids as they are exhibited in aqueous solutions. The discussion of these results with reference to the constitution of these compounds, will follow in another paper.

2. From his recent determinations the author has calculated the following numbers:—

	Heat-units.		Heat-units.
(SO_2,Aq) .... =	7968	$(Na_2S_2O_3Aq,2HClAq)$. =	− 2176
(SO_2Aq,Cl_2) .... =	73907	(K_2SO_4,SO_2) .... =	0
$(Na_2S_2O_3Aq,4ClOHAq)$ =	251624	(K_2SO_4,Aq) .... =	− 6384
$(2Na_2S_2O_3Aq,I_2)$ ...... =	7954	$(K_2S_2O_6,Aq)$ .... =	−12986

and from results already published—

	Heat-units		Heat-units.
(H_2,O) .... =	68357	$(2\bar{N}aAq,SO_2Aq)$ ...... =	28970
(I,H,Aq) .... =	13171	$(2\bar{N}aAq,S_2O_5Aq)$ ...... =	27070
(Cl,H,Aq) .... =	39315	$2(\bar{N}aAq,HClAq)$ ...... =	27480
(Cl,O,H,Aq) .... =	28322	$2(\bar{N}aAq,HIAq)$......... =	27350
$(\bar{N}aAq,SO_3Aq)$......... =	14754	$(\bar{N}aSO_3Aq,2HClAq)$ .. =	− 978

and from Favre and Silbermann's determination of the heat of combustion of sulphur: $(S_2,O_2) = 71072$ heat-units.

3. As the evolution of heat in the reaction of chlorine upon an aqueous solution of sulphurous acid may be expressed by—

$$(SO_2Aq,Cl_2) = (SO_2Aq,O) - (H_2,O) + (Cl_2,H_2,Aq),$$

we have $(SO_2Aq,O) = 63634$ heat-units, and

$$(SO_2,O,Aq) = (SO_2Aq,O) + (SO_2,Aq) = 71332 \text{ heat-units.}$$

From this follow the total heats of formation of sulphurous and sulphuric acids—

$$(S,O_2,Aq) = (S,O_2) + (SO_2,Aq) = 78770 \text{ heat-units,}$$

and—

$$(S,O_3,Aq) = (S,O_2) + SO_2,O,Aq) = 142404 \quad ,,$$

4. The heat-modulus of the decomposition of potassium dithionate is $= 0$, or $(K_2SO_4,SO_2) = 0$, and therefore $(K_2,O_2,SO_2) = (K_2,O_2,2SO_2)$. These reactions may be split up into—

$$(K_2,O_2,SO_2) + (K_2SO_4,Aq) = K_2,O,Aq) + (SO_2,O,Aq) \\ + (2\bar{K}Aq,SO_3Aq),$$

and—

$$(K_2,O_2,2SO_2) + (K_2S_2O_6,Aq) = (K_2,O,Aq) + 2SO_2,O,Aq) \\ + (2\bar{K}Aq,S_2O_5Aq).$$

On subtracting these two equations from each other, the first and third terms, being equal, disappear; all the remaining terms are known, except $(2SO_2,O,Aq)$, which can now be calculated—

$$(2SO_2,O,Aq) = 68950 \text{ heat-units,}$$

and—

$$(S_2,O_5,Aq) = (2SO_2,O,Aq) + 2(S,O_2) = 211094 \text{ heat-units,}$$

which represents the total heat of formation of dithionic acid.

5. The heat of neutralisation of thiosulphuric acid cannot easily be determined directly, on account of its great tendency to decompose; but by adding the neutralisation heat of hydrochloric acid to the quantity of heat absorbed in the decomposition of sodium thiosulphate—2176 heat-units—the author obtains 29656 heat units, a number not differing much from the neutralisation heat of sulphurous acid—28970 heat-units—which number is accordingly adopted as the neutralisation heat of thiosulphuric acid. By introducing this value into the equation expressing the reaction of hypochlorous acid upon sodium thiosulphate—

$$(Na_2S_2O_3Aq,4ClOHAq) = \begin{cases} (S_2O_2Aq,O_4) \\ 2(\overline{Na}Aq,SO_3Aq,2HClAq) - (2\overline{Na}Aq,S_2O_2Aq) \\ 4(Cl,H,Aq) - 4(Cl,O,H,Aq), \end{cases}$$

we obtain for the heat liberated in the oxidation of thiosulphuric to sulphuric acid—

$$(S_2O_2Aq,O_4)' = 209070 \text{ heat-units},$$

and by means of the equations—

$$\begin{aligned} 2(S_2,O_3,Aq) &= (S_2,O_2,Aq) + (S_2O_2Aq,O_4) \\ (S_2,O_2,Aq) &= (S,O_3,Aq) + (SO_2,Aq,S) \end{aligned}$$

we obtain further—

$$\begin{aligned} (S_2,O_2Aq) &= 75738 \text{ heat-units.} \\ (SO_2Aq,S) &= -\ 3032 \quad ,, \\ (SO_2,S,Aq) &= +\ 4666 \quad ,, \end{aligned}$$

for the heat reactions implied in the formation of thiosulphuric acid.

6. The heat produced in the oxidation of thiosulphuric acid to *tetrathionic* acid can be calculated from the heat liberated in the reaction of iodine upon sodium thiosulphate—

$$2Na_2S_2O_2Aq,I_2 = \begin{cases} (T_2,H_2Aq) + 2(NaAq,HIAq) \\ (2S_2O_2Aq,O) - (O,H_2) \\ (2NaAq,S_4O_5Aq - 2(2\overline{Na}Aq,S_2O_2Aq). \end{cases}$$

By assigning to these reactions their values, as given above (the neutralisation heat of tetrathionic acid is taken as equal to that of dithionic acid, 27070 heat-units), we have—

$$2(S_2O_2Aq,O) = 53489 \text{ heat-units}.$$

from which, by the equations—

$$\begin{aligned} (S_4,O_5,Aq) &= 2(S_2.O_2,Aq) + (2S_2O_2Aq,O) \\ (S_4,O_5,Aq) &= 2(S,O_2) \qquad + (2SO_2,O,S_2,Aq) \end{aligned}$$

the affinities satisfied in the formation of tetrathionic acid are found—

$$(S_4,O_5,Aq) = 204965 \text{ heat-units}.$$

7. If we consider thiosulphuric acid to be formed by the reaction of

sulphurous acid, sulphur, and water, we obtain the effect of the second atom of sulphur by the equation—

$$(SO_2,Aq) - (SO_2,S,Aq) = 7698 \text{ heat-units} - 4666 \text{ heat-units} = 3032 \text{ heat-units}.$$

and considering tetrathionic acid to be formed in an analogous way from dithionic acid, we obtain the effect of the two additional atoms of sulphur from the equation—

$$(2SO_2,O,Aq) - (2SO_2,O,S_2Aq) = 68950 \text{ heat-units} - 62821 \text{ heat-units} = 6129 \text{ heat-units}.$$

As $6129 = 2 \times 3064$, we see that the two atoms in the second case have very nearly double the effect of the one atom in the first case, so that we may conclude that, for *every additional atom of sulphur, the total heat of formation of the sulphur-acids is diminished by* 3032 *to* 3064 *heat-units.*

The author has accordingly not thought it necessary to determine experimentally the heats of formation of trithionic and pentathionic acids, which have been calculated from those of dithionic and tetrathionic acids. The results have been summed up in the following tables :—

TABLE I.

	Heat-units.
(S,O_2,Aq) .... =	78770
(S_2,O_2,Aq) .... =	75738
(S,O_3,Aq) .... =	142404
(S_2,O_5,Aq) .... =	211094
(S_3,O_5,Aq) ...... =	208030
(S_4,O_5,Aq) .... =	204965
(S_5,O_5,Aq) .... =	201901

TABLE II.

	Heat-units.
(SO_2,Aq) .... =	7698
(SO_2,S,Aq) ...... =	4666
(SO_2,O,Aq) ...... =	71332
$(2SO_2,O,Aq)$ .... =	68950
$(2SO_2,S,O,Aq)$ .. =	65886
$(2SO_2,S_2,O,Aq)$ .. =	62821
$(2SO_2,S_3,O,Aq)$ .. =	59757

TABLE III.

	Heat-units.
Sulphurous acid (SO_2,O,H_2,Aq) .... =	76055
Thiosulphuric acid $(SO_2,S,O.H_2,Aq)$ ...... =	73023
Sulphuric acid (SO_2,O_2,H_2,Aq) .... =	139869
Dithionic acid $(2SO_2,O_2,H_2,Aq)$ .... =	137307
Trithionic acid $(2SO_2,S,O_2,H_2,Aq)$ .... =	134243
Tetrathionic acid $(2SO_2,S_2,O_2,H_2,Aq)$...... =	131178
Pentathionic acid $(2SO_2,S_3,O_2,H_2,Aq)$ .... =	128114

If we suppose the acids to be formed from sulphurous acid and hydroxyl, for which the author has found—

$$(H_2,O_2,Aq) = 45045 \text{ heat-units},$$

we obtain for—

Sulphuric acid (SO_2Aq,H_2O_2Aq)...... = 86946 heat-units.
Dithionic acid $(2SO_2Aq,H_2O_2Aq)$...... = 76886 „

The corresponding values for every other polythionic acid with

n sulphur-atoms, can be calculated by subtracting $(n-2)$ 3064 heat-units from that of dithionic acid.

R. S.

Rapid Dissemination of Gases of Different Specific Gravities.

By M. v. PETTENKOFER (N. Repert. Pharm., xxii, 111).

THE Marien-well at Marienbad is built over with a plank-house, and is 23·7 meters long, and 11·4 broad, the water being about two meters deep on an average.

Samples of gas were taken at different heights above the surface of the water, and were found by a rough process of analysis to contain the following quantities of carbon dioxide.

Gas collected below surface of well-water	70 per cent.
„ 5 centimeters above well-water ..	31 „
„ 25 „ „ „ ..	23 „
„ 100 „ „ „ ..	2 „
„ 145 „ „ „ ..	inappreciable.

Hence, notwithstanding the rapid evolution of gas in the well, downward motion of the air into the heavy gases evolved must take place with great rapidity.

C. R. A. W.

Supersaturated Saline Solutions. By C. TOMLINSON (Chemical News, xxvii, 145).

THE author reviews the many questions at issue respecting the determination of the crystallisation of supersaturated solutions, and virtually admits that the question, "What is a nucleus?" is not yet satisfactorily answered.

In opposition to the experiments of Gernez, Violette, and especially of Liversidge, who state "that the only nucleus capable of suddenly crystallising any one of such solutions, is a salt of the same kind as that dissolved," he contends that there are many nuclei, and reiterates his earlier experiments, in which thin films of oil were found to cause the solidification of a great many supersaturated solutions.

He also replies briefly to the objections which have been raised against conducting the experiments in the open air, and points out that, if the crystallisation of the solution requires absolutely the intervention of a similar crystal, we should be reduced to the dilemma of supposing that there must be floating in the air specimens of all kinds of salts that form supersaturated solutions, and crystallise by the introduction of a solid nucleus: whereas, there are some such salts which cannot exist in the presence of atmospheric oxygen.

J. W.

On the Supposed Action of Liquid Films upon Supersaturated Solutions. By D. GERNEZ (Compt. rend., lxxv, 1705—1708).

VAN der Mensbrugghe and Tomlinson state (*Phil. Mag.*, lxiv, 223), that when a film of a liquid of feeble surface-tension is placed on the

surface of a supersaturated solution, or when a solid is coated with such a film, and immersed in the solution, crystallisation takes place. Gernez contradicts this statement on the strength of the following experiments. A supersaturated solution of sodium sulphate containing two parts of the 10-atom salt to one of water, was filtered into flasks which had been carefully cleansed with oil of vitriol, and then with water. After the flasks had remained at rest several hours, films were formed on the surface of 54 portions of the solution on adding a small quantity of 18 different substances, each experiment being repeated three times. The liquids used were :—oil of turpentine, the essential oils of lemon, orange, rosemary, cajeput, lavender, and anise-seed; olive-oil, linseed-oil, oil of sweet almonds, castor-oil, cod-liver oil, fish-oil; petroleum, benzene, creasote, methylic and ethylic alcohol. In no instance did crystallisation take place, even after a week. The same result was obtained with sodium acetate, potassium-alum, ammonium-alum, magnesium sulphate, sodium thiosulphate and sodio-potassium tartrate, the total number of experiments being eight hundred.

As to the second proposition: glass rods were smeared with olive-oil and immediately plunged into supersaturated solutions of sodium acetate, sodium thiosulphate, and sodio-potassium tartrate, each experiment being repeated six times, without any crystallisation taking place.

Gernez believes that the crystallisations of sodium sulphate obtained by van der Mensbrugghe and Tomlinson were due to small particles of that salt which, he thinks, are always floating in the air, even of the country, or, in the case of the other salts, to particles disseminated in the atmosphere during the preparation of the experiments.

B. J. G.

Reply to Gernez's Criticism of van der Mensbrugghe and Tomlinson's Theory of the Action of Liquid Films. By G. van der Mensbrugghe (Compt. rend., lxxvi, 45—48).

An account is given of the part taken by van der Mensbrugghe and Tomlinson respectively, in the investigation criticised. The former, believing that there was an intimate connection between the contractile forces of liquids and the phenomena exhibited by supersaturated solutions in contact with liquid films, communicated his ideas in four propositions to Tomlinson, who then made several new experiments, and repeated some old ones. Their joint account was written before the results were quite satisfactory, because they hoped thereby to obtain the co-operation of other physicists. They by no means asserted, as Gernez conceives, that the matter was set at rest. Gernez states that he followed Tomlinson's directions implicitly, but it appears that his solution of sodium sulphate consisted of 2 parts of salt to 1 part of water, whereas the authors employed a solution containing 1 part of salt to 1 part of water. They found, in fact, that it was more difficult to induce crystallisation in the stronger solution than in the weaker, thus showing that surface-tension had evidently some action, a point not touched by Gernez, who used a solution of one strength only. As to the assertion that greased solids when introduced into supersaturated solutions of

sodium acetate, sodium thiosulphate, and sodio-potassium tartrate produced no crystallisation, it is replied that the surface-tension of these solutions not having been given, it is impossible to form any proper judgment from the results. It is asked, too, why sodium sulphate was not tried in these experiments. Gernez rejects the surface-tension theory only to fall back upon one that supposes the crystallisations to be caused by particles of the salts floating in the air or contained in the oils, &c., employed. The author replies as to the first idea, that this is not opposed to his own view, since he believes such particles to be covered with a film of greasy matter. Indeed, Tomlinson (*Phil. Mag.*, 1868, 665; 1870, 65), showed that chemically pure crystals would not produce crystallisation. Moreover, every care was taken to prevent the interference of dust. The solutions were made in a large test-tube, filtered while boiling into flasks, then boiled again, the flasks covered with watch-glasses, and taken into the open country air. Finally, it is asked, if the oils, &c., employed, contained traces of crystalline substances, why were not the strong solutions as easily crystallised as the weak?

B. J. G.

On the Supposed Action of Liquids of Feeble Surface-tension upon Liquids of Strong Surface-tension. By D. Gernez (Compt. rend., lxxvi, 89—92).

Van der Mensbrugghe (*Compt. rend.*, lxxiv, 1038), announced, as "a new principle in physics," that "whenever a liquid having a strong surface-tension and containing gas is placed in contact with a liquid of feeble surface-tension, a disengagement of the dissolved gas takes place." The three chief cases in which he considered that this principle came into play were—(1) The disengagement of gas by agitating a liquid with which a small quantity of another liquid of feebler surface-tension has been mixed; (2) The disengagement of gas at the plane of separation of two liquids of different surface-tension; (3) The disengagement of gas (from a liquid containing it) by contact with a solid which has been slightly greased, the grease being supposed to represent the liquid of feebler surface-tension in the second case. Gernez has made experiments under each of these conditions, with the following results:—

(1.) Distilled water, it is true, when shaken with a few drops of alcohol, effervesces briskly, whereas the water or the alcohol, when shaken alone, gives no effervescence. But this was proved to be due to the expulsion of the air temporarily dissolved by the agitation. Nine litres of water containing a little alcohol were agitated in a flask furnished with a pierced cork, carrying a bent tube containing water, so that the least pressure might be indicated. Although there was a brisk effervescence, the index showed a slight absorption rather than a disengagement of gas. The same result followed when the alcohol was replaced by creasote, or the oils of turpentine, lavender, olive, linseed, colza, and sweet almonds; moreover, after a hundred agitations, the effervescence was as brisk as at first, and no diminution of gas was observed when the water had been previously boiled.

(2.) The conditions of the second case were purposely exaggerated by employing a saturated solution of carbon dioxide, upon which were placed, successively, liquids of a greater density, such as carbon sulphide and chloroform; of a less density, such as the fixed and volatile oils; and, lastly, liquids miscible with the solution, such as alcohol, ether, and creasote. In no case was any gas given off when the liquids had been carefully filtered and then kept from contamination by the air.

(3.) Having shown in (2) that such a fatty layer as that mentioned in van der Mensbrugghe's third case could have no action upon the gas, and having pointed out (*Compt. rend.*, lxiii, 883), that solids, the surfaces of which have been deprived of gas, are also inactive, it was hardly necessary to ascertain if the two together could produce an effect unproducible by either singly. The experiment being made, however, it completely contradicted van der Mensbrugghe's assertion. A saturated solution of carbon dioxide was covered with a layer of olive-oil, and this with one of alcohol. Glass rods, which had been deprived of adhering air by keeping in alcohol, were put slowly into the oil, and then passed into the solution. In no case was there the least disengagement of gas.

B. J. G.

On Prince Rupert's Drops and the Annealing of Glass.

By V. DE LUYNES (Compt. rend. lxxvi, 346).

HITHERTO it has been supposed that the explosions of Prince Rupert's drops were caused by the state of forced expansion of their interior. From the following experiments, however, the author concludes that the phenomenon is to be ascribed to the abnormal state of expansion of the external layers. He found that nearly the whole of the tail may be dissolved by hydrofluoric acid without explosion, which, however, takes place as soon as the root of the tail is attacked. When, on the other hand, the thick end is first exposed, the drop will gradually dissolve, without any sudden disaggregation of the whole. These experiments prove that the root of the tail is a point of primary importance for the molecular equilibrium of a drop. Now as the external parts, having been cooled more rapidly, must be in a more abnormal state of expansion than the internal parts, it follows that the external layers which all meet in the root of the tail, must by the destruction of this root be suddenly relieved from a resistance which is offered to their return into their normal state of expansion; and hence we may understand why the sudden removal of this resistance is followed by an explosive destruction of the whole structure.

For a similar reason the explosion takes place always when the molecular equlibrium of the constrained layers of a drop is suddenly disturbed by cutting them with a saw.

After the rupture, the contraction will be greatest there where the particles had been most displaced from their natural position. For this reason the section formed by cutting a drop with a saw will present a conical surface, covered with a multitude of fine needles, all of which have their summits turned towards the thick end, whilst they are directed towards the tail when this explosion has been brought about

by first destroying the tail. The conical shape of the face of rupture, and the needles directed towards the apex of the cone are frequently observed in the case of unannealed glass rods, also of glass tubes which have been immersed in water while in the melted state, and in various other cases.

R. S.

Inorganic Chemistry.

A New Mode of Producing Ozone. By A. BOILLOT (Compt. rend., lxxv, 1712).

A TUBE 0·45 meter in length, and 10 mm. interior diameter, is placed within another tube, 0·40 meter in length, and 15 mm. interior diameter. The annular space between the two tubes is filled with finely powdered gas-carbon The inner tube contains the same kind of carbon in small pieces. Through the inner tube is passed a stream of dry oxygen, a current of induced electricity, derived from a Ruhmkorff coil, working with five Bunsen's elements, being at the same time sent through the apparatus. The mean of two experiments gave 0·0435 gram of ozone per litre of oxygen.

B. J. G.

On Sulphurous Acid and Chlorosulphuric Acid. Combination of Chlorine and Hydrogen in the Absence of Light. By M. MELSENS (Compt. rend., lxxvi, 92—94).

I. THE author finds that sulphurous acid and dry chlorine combine even in the absence of light, if the gases are passed into glacial acetic acid. Chloracetic acids and chlorosulphuric acid are produced, the latter of which may be separated by fractional distillation; bromosulphuric acid could not be obtained by this method.

II. Chlorosulphuric acid can also be produced by causing charcoal (*braise*), purified by repeated washing and calcination, to absorb chlorine and sulphurous acid successively.

III. When charcoal absorbs dry chlorine, the temperature rises, and if dry hydrogen be brought in contact with the carbon, saturated with chlorine, notable quantities of hydrochloric acid are produced, whilst chlorine is at the same time given off, and the temperature falls.

IV. Water acts on charcoal saturated with chlorine, forming hydrochloric acid and carbonic acid, and producing a slight elevation of temperature.

V. The author has also found that the process for the preparation of sulphurous acid, indicated by M. Dumas, of heating together sulphur and concentrated sulphuric acid, may be conveniently conducted in vessels of cast-iron, or even of glass, if fragments of pumice be introduced into the mixture. His experiments on the boiling point of liquid sulphurous acid gave results similar to those published in 1862 by

Regnault, and the determination of the vapour-tension at 100° agrees sensibly with the number given by Regnault's formula.

C. E. G.

Selenic Acid and Selenates. By v. GERICHTEN (Deut. Chem. Ges. Ber., vi, 162—165).

PURE selenic acid is readily obtained by the following method. Selenium, which may contain sulphur, is oxidised with nitric acid, and the selenium dioxide is dissolved in caustic potash, and completely oxidised by chlorine. The solution is precipitated with a barium-salt, and the precipitate treated with a cold solution of potassium carbonate, by which by far the greater portion of the selenate is decomposed. Thus 24·23 grams of pure barium selenate yielded on reprecipitation 23·81 of the pure salt, while from a mixture of 0 64 of barium selenate, and 0 78 of barium sulphate, 0 59 of pure selenate were obtained again. To prepare the free acid, the potassium salt is converted into the lead-salt, and the latter decomposed with hydrogen sulphide.

The following mixed sulphates and selenates were prepared, and found to be isomorphous with the corresponding pure sulphates and selenates :—

$$(1.)\ \begin{array}{l}\left.\begin{array}{r}SO_2\left\{\begin{array}{l}O\\O\end{array}\right.\\ SeO_2\left\{\begin{array}{l}O\end{array}\right.\end{array}\right\}M'''\\ \qquad\quad\;\; O \quad M\end{array} \text{ and } \begin{array}{l}\left.\begin{array}{r}SeO_2\left\{\begin{array}{l}O\\O\end{array}\right.\\ SO_2\left\{\begin{array}{l}O\end{array}\right.\end{array}\right\}M''',\\ \qquad\quad\;\; O \quad M\end{array}$$

in which M represents potassium or ammonium, and M''' aluminium or chromium.

(2.) $K_2SeO_4 + M''SO_4 + 6H_2O$ and $K_2SO_4 + M''SeO_4 + 6H_2O$, M'' representing nickel, cobalt iron, zinc, manganese, cadmium, copper, or mercury.

C. S.

Nitrification of Vegetable Earth. By M. BOUSSINGAULT (Compt. rend., lxxvi, 22—29).

To ascertain if atmospheric nitrogen takes any part in the nitrification of a vegetable soil, the author took two flasks of about 86 litres capacity, and placed in each 100 grams of vegetable soil, mixed with three times its weight of pure sand, and moistened; one mixture contained in addition 5 grms. of cellulose. The flasks were closed with caoutchouc, and left for eleven years in a cellar. At the end of this time the contents were analysed. The simple mixture had lost 4 per cent. of its total nitrogen, and 16 per cent. of its carbon, and gained ·6149 grm. of nitric acid. The mixture with cellulose had lost 2 per cent. of its nitrogen, and 43 per cent. of its carbon, and had gained ·5591 grm. of nitric acid. In both cases there was a loss of nitrogen, and therefore no gain from the atmosphere. The amount of nitrates formed was equal to that in a good French nitre-bed.

The author believes that in the tropics the continual thunderstorms play a principal part in the formation of nitric acid, and seems disposed to attribute the vast stores of nitrates in Peru to such an origin.

R. W.

The Vapour-density of Potassium. By J. DEWAR and W. DITTMAR (Chemical News, xxvii, 121).

THE communication is only a preliminary notice. The vessel in which the potassium vapour was generated consisted of an iron bottle, about 200 c.c. capacity, provided with a well ground neck, pierced with a canal of about 2 mm. in diameter. The interior of this receptacle was first deoxidised at a red heat with dry hydrogen, then about 200 grams of mercury were introduced, and the bottle was immersed in molten zinc. When the larger portion of the mercury had distilled, the neck was withdrawn, and a small iron test-tube, containing 4 or 5 grams of potassium quickly dropped into the bottle; the neck was then replaced, and the bottle having been wholly immersed in the zinc, the fire was urged so as to bring the zinc rapidly to the boiling temperature, 1040°. When the distillation of the potassium ceased, the nozzle was closed by means of a ground-in wire plug, and dipped into a vessel containing mercury.

The plug was afterwards withdrawn beneath the surface of water, and the hydrogen formed by the action of the water upon the potassium having been pumped out into a endiometer, the volume of the potassium vapour was calculated. The results of the observations show that the density of potassium vapour does not exceed 45 times that of hydrogen, and that therefore the molecule of potassium doubtless consists of two atoms (K_2).

J. W.

The Vapour-density of Phosphorus Pentachloride. By A. WURTZ (Compt. rend., lxxvi, 601—610).

THE researches of Cahours upon the vapour-density of phosphorus pentachloride have shown that this substance, in the gaseous state, does not conform to the general law of a condensation of the molecule in two volumes. The anomaly has been frequently explained by assuming that a partial dissociation takes place even at low temperatures. If this explanation be correct, it is probable that a normal number would be obtained, if it were possible in any way either to diminish or to prevent the phenomenon of dissociation, and the experiments of Wurtz were undertaken with this end in view.

In the first place the boiling point of the pentachloride was lowered by diminishing the pressure, or what amounts to the same thing, advantage was taken of the vapour-tension at a temperature below the boiling point, to diffuse a certain quantity of the substance throughout a large volume of air. The operation was conducted in a flask placed in a paraffin-bath, and the point of the flask was sealed as soon as the last particle of pentachloride had disappeared. The flask was weighed and the residual air calculated in the usual manner.

The vapour of the perchloride was thus diffused into a determinate volume of air, the mixture supporting the pressure of the atmosphere at the moment of closing the flask; the partial pressure to which the perchloride itself was subjected was subsequently calculated.

Eleven experiments were made, three of which are given here as examples—

	Vol. of the vapour. 0° 760.	Residual air. 0° 760.	Density of the vapour.	Partial pressure.	Temperature.
	c c.			mm.	
I	85·1	123·0	6·70	311	145°
II........	39·75	165·15	6·47	148	137°
III	52·8	179·0	6·63	170	129°

As the result of the foregoing experiments, the vapour-density of the perchloride was ascertained to be about 6·5, referred to air as unity.

The highest number obtained by Cahours for the density of the perchloride was 5·078, the density having been taken at the ordinary pressure and at 182°. By lowering the pressure it is possible therefore to raise this figure to 6·5, a number situated much nearer to 7·217, the density calculated for a two-volume condensation, than to 3·61, which would be the density calculated for a condensation in four volumes. Seeing that the question was not satisfactorily resolved, another series of experiments was undertaken, in which account was taken of the influence which the medium may exert upon dissociation itself, according as it is possible or impossible to saturate it with the vapour of the products of dissociation. The pentachloride was therefore diffused into a space already saturated or filled with the vapour of phosphorus trichloride. The experiments required great care in execution, but were brought to a satisfactory termination. The calculations from the second weighing of the flask gave of course the joint weight of the vapour of the pentachloride and trichloride, and it became necessary to analyse the residue in order to ascertain the proportions of the two chlorides. The total weight of the chlorides being known, the chlorine was estimated and the phosphorus calculated by difference; and since two determinate weights of chlorine and phosphorus correspond with a certain mixture of pentachloride and trichloride, the ratio between the chlorides was easily ascertained.

The following table is a summary of the experiments:—

	I.	II.	III.	IV.	V.	VI.
	c.c.					
Volume of the vapour of pentachloride ..	49·2	83·4	55·5	62·2	77·1	39·5
Density of the vapour of pentachloride ..	7·25	7·38	7·74	7·06	7·03	8·30
	mm.					
Partial pressure	194	338	168	271	343	174

	VII.	VIII.	IX.	X.	XI.	XII.
	c.c.					
Volume of the vapour of pentachloride ..	121·8	94·4	54·4	90·9	75·6	97·8
Vapour density of pentachloride	6·88	7·16	7·44	6·80	7·0	6·68
	mm.					
Partial pressure	411	394	214	413	318	423

It will be observed that the numbers obtained in this series of twelve experiments are higher than those previously obtained, notwithstanding that the density was taken at a temperature above the boiling point of the perchloride, indeed closely approximating to the temperature at which Cahours observed the density 5 078.

Seven of the numbers sensibly agree with the theoretical one, 7·217, while the mean experimental density calculated from the whole is 7·226.

The identity of these two numbers is perfect, and the following conclusion may therefore legitimately be drawn; that the vapour of phosphorus pentachloride presents a normal condensation in two volumes, when the dissociation of the molecule is successfully prevented.

The author considers the pentadicity of phosphorus as definitely settled.

J. W.

Separating Gold from Silver Chloride. By A. Leibius (Chemical News, xxvii, 121).

The silver chloride, formed in the purification of argentiferous gold by means of chlorine gas, contains an appreciable amount of gold, to such an extent indeed, that the silver bullion obtained by the reduction of the chloride often contains as much as 18 per cent of gold. The processes generally adopted for the removal of this gold do not give satisfactory results, and the author was therefore induced to make some experiments upon the subject, the results of which led to the adoption of the following method:—The fused chloride is covered with a layer of borax, one-eighth to one-quarter inch in thickness, and sodium carbonate is gradually added on the top of this layer, in quantity varying from 16 to 20 ozs. per 230 ozs. of silver chloride operated on. The chloride is not stirred, but the metallic gold is allowed to subside to the bottom of the receptacle. 20 oz. of soda will generally produce a gold button weighing about 35 oz., assaying from 870 to 880, while the silver bullion subsequently obtained will contain 2 to 5 parts of gold in 10,000 parts.

A second treatment with a much smaller quantity of soda renders the silver perfectly free from gold.

J. W.

Combination of Phosphorus with Zinc and Cadmium. By B. Regnault (Compt. rend., lxxvi, 283—286).

In this paper the author describes additions to his former investigations on this subject. The following have been already described.

A compact and crystalline phosphide of zinc, Zn_3P_2.

A crystalline phosphide, ZnP.

An amorphous pulverulent phosphide, Zn_3P_2.

A phosphide crystallised in fine needles, varying in colour from pale

yellow to orange-yellow or vermilion-red. The composition was not formerly given, but the body has now been examined afresh.

When vapour of phosphorus is allowed to pass over metallic zinc, or zinc oxide or carbonate, at a low red heat, the mass becomes incandescent, and after the sublimate has cooled, a metallic-looking mass, particularly crystallised, is obtained. This contains some of the needle-shaped crystals just mentioned. If these last are moderately heated in a closed tube, they all turn red, and keep that colour. Strongly heated, they lose phosphorus and acquire a metallic aspect. The composition of the crystals thus reduced is Zn_3P_2.

In the air the crystals burn brightly, and are converted into zinc phosphate.

Sulphuric and hydrochloric acids scarcely dissolve them at all; but nitric acid attacks them strongly, and they detonate when mixed with nitrates and chlorates.

By washing repeatedly with dilute hydrochloric acid, the phosphate of zinc which is formed with the phosphide when the vapour of phosphorus is passed over oxide of zinc, is removed. The phosphide is then found to have the composition ZnP_2.

The phosphides of cadmium are prepared in a manner similar to that mentioned above for zinc. The phosphides that have been obtained by the present author aie Cd_3P_2 and CdP_2.

The former agrees very exactly in its appearance and properties with the corresponding zinc phosphide. It is metallic-looking, and readily combines with oxidating agents. However, it dissolves readily in weak acids, and gives off phosphuretted hydrogen not spontaneously inflammable.

The phosphide CdP_2 also corresponds closely in properties, and generally in appearance, with ZnP_2. It is most easily prepared by heating in a retort a mixture of ammonium phosphate, or phosphate of mercury or tin, with cadmium carbonate and carbon. The volatilised products having been condensed, it is easy to separate the cadmium phosphide by washing it out with dilute hydrochloric acid.

The phosphide is generally obtained in small bright red crystals. It is, however, sometimes obtained in small indigo-blue scales or plates. The chief difference between the properties of this substance and of zinc phosphide is, that while the latter is scarcely soluble in boiling hydrochloric acid, the former is readily attacked; phosphuretted hydrogen is given off, and the remaining liquor contains cadmium chloride and hypophosphorous acid, and holds a beautiful yellow body in suspension.

This yellow body contains 93 p.c. of phosphorus.

J. T. B.

On the Solution of Gases in Iron, Cast-Iron, and Steel. By L. TROOST and P. HAUTEFEUILLE (Compt. rend., lxxvi, 482—485 and 562—566).

IT is generally admitted that these metals, at a high temperature, possess the property of dissolving gases which they evolve in part as

the temperature sinks. The authors have arrived at the conclusion, as the result of their experiments, that the disengagement of gas which is observed in making large castings and in other metallurgical operations, is not due to this cause alone, inasmuch as the phenomenon can be produced under circumstances in which the variation of temperature is too slight to affect appreciably the solubility of the gases; and moreover, the disengagement of gas is frequently attended by change in the composition of the metal operated upon.

In a preliminary series of experiments, the authors found that cast-iron kept in a state of fusion in a porcelain boat placed in a tube of porcelain, under much reduced pressure, continued to evolve gas at the end of the third day. The same metal fused in an atmosphere of carbon oxide or hydrogen, behaved as in a partial vacuum. The gas given off was in all cases carbon oxide; and the production of this gas was found to be due to the action of the fused metal upon the porcelain boat, the metal gradually becoming richer in silicium and poorer in carbon, till in some cases the proportion of silicium amounted to as much as 8 p.c. These experiments demonstrated the fact that at temperatures above the melting-point of cast-iron, carbide of iron possesses the property of reducing silica.

A second series of experiments was made with the object of ascertaining the increase of silicium in cast-iron fused under a pressure of carbon oxide approximating to that which exists in iron furnaces. In these experiments the authors employed crucibles of gaize, a highly refractory substance containing much silica and but little alkali.

A grey cast-iron, containing 0·21 p.c. of silicium and 5·32 p.c. of carbon, was fused in a very thick crucible of gaize placed inside a plumbago crucible lined with gas-carbon, the metal thus being in contact with an atmosphere of carbon oxide and hydrogen as in an ordinary coke fire. After 24 hours' fusion, it was found that the gaize had been strongly attacked by the fused metal, which had become richer in silicium, whilst an acid ferrous silicate was formed at the same time. Some globules of the metal had eaten holes more than 2 centimeters deep in the sides of the crucible. Similar experiments were made with steel. The results of analyses of the metal before and after experiment were as follows:—

	Silicium.	Carbon.
Cast-iron employed	0·21	5·32
„ after 48 hours' fusion in porcelain	0·87	5·20
„ after 24 hours' fusion in gaize	1·07	3·90
„ globule imbedded in gaize	3·40	—
Cast-steel employed	0·10	1·54
„ after 24 hours' fusion in a Hessian crucible	0·26	0·74
„ after 24 hours' fusion in gaize	0·80	0·70

Hence, in order to avoid the introduction of silicium into these metals, it is necessary to fuse them in vessels of lime or magnesia.

The reaction which takes place in these experiments must, according to the authors, go on to some extent in the blast furnace and tend to increase the proportion of silicium in the cast-iron produced; but they do not regard it as the principal cause of the production of iron rich in

silicium; for the action of carbide of iron on silica is slow, and the more so the more highly basic the slags present; experiment, indeed, has shown that cast-iron fused in lime or in highly basic calcium silicate loses silicium. The chief cause lies rather in the action of alkali-metals, which are always present, upon silicates. The influence of these metals becomes evident on heating a mixture of potassium carbonate, carbon, iron filings, and silica in a wind-furnace, and thus bringing together iron, silica, and the vapour of potassium. Under these conditions the authors obtained a cast-iron containing 5·16 p. c. of silicium and 2·94 p. c. of carbon.

The preceding experiments show that the gas given off by fused cast-iron is frequently due to the action of carbide of iron on silica. Gases, may, however, be extracted from the fused metal without its attacking the walls of the crucible on the slag in contact with it.

Cast-iron raised to a high temperature in a carbon boat in an atmosphere of hydrogen undergoes tranquil fusion; there is no disengagement of gas and no projection of the metal. But if after it has remained for some time in this atmosphere the pressure of the hydrogen be rapidly diminished, the disengagemnt of gas is rendered evident by the projection of globules of metal and particles of graphite, and if the temperature be allowed to fall at the same time, the metal solidifies during the disengagement of gas, and the surface of the ingot is rough. The solubility of hydrogen in cast-iron is much diminished by the presence of phosphorus or silicium (especially the latter) in the metal.

Carbon oxide is much less soluble than hydrogen in cast-iron, more especially in highly carburetted iron.

These results were confirmed by the authors by extracting the gases dissolved or enclosed in pig-iron. A cylinder of the metal weighing 500 grams heated to 800° in a vacuum gave off in 190 hours 16·7 c.c. of gas consisting of

Carbon dioxide.	Carbon oxide.	Hydrogen.	Nitrogen.
0·6	2·8	12·3	1·0

The greater part of the carbon oxide was disengaged in a few hours, while the hydrogen was much more forcibly retained.

The same cylinder of cast-iron was afterwards heated to 800° for 48 hours under a pressure of 770 mm.: (1) in hydrogen, and (2) in carbon oxide, and after each operation placed in a vacuum for 170 hours. The gases extracted in the two cases were—

	Carbon oxide.	Hydrogen.	Nitrogen.	
(1.)	1·1	44·0	1·5	= 46·6 c.c.
(2.)	14·7	1·5	0·7	= 16·9 „

Hence the order of solubility is the same as in the fused metal.

To ascertain the effect of different proportions of carbon in the metal on the solubility of the gases, the authors made comparative experiments with cast-steel and soft iron. Cylinders of these metals, each weighing 500 grams, when heated to 800° in a vacuum, gave off the following gases:—

	Carbon dioxide.	Carbon oxide.	Hydrogen.	Nitrogen.	
Cast-steel	0·05	1·4	0·5	0·25 =	2 2 c.c.
Soft iron ...	2·20	10·8	4·4	1·1 =	18·5 „

These cylinders were heated to 800°: (1) in hydrogen, and (2) in carbon oxide and afterwards placed in a vacuum, as in the case of the cast-iron cylinder. The gases extracted were—

		Carbon oxide.	Hydrogen.	Nitrogen.	
From cast-steel	(1.)	0 9	6·4	0·5 =	7·8 c.c.
	(2.)	2·0	0·8	0·4 =	3·2 „
From soft iron	(1.)	0 6	10·0	3·3 =	13·9 „
	(2.)	13·7	0·2	0·1 =	14·0 „

Steel retains the last traces of hydrogen much more forcibly than cast-iron, notwithstanding that when saturated with the gas it gives off a portion at the ordinary temperature, in this respect resembling palladium.

Soft iron retains carbon oxide more forcibly than it retains hydrogen, contrary to what is observed with cast-iron and steel.

J. R.

Mineralogical Chemistry.

Graphite. By C. Rammelsberg (Deut. Chem. Ges. Ber., iv, 187).

The purer varieties of natural graphite often sustain on ignition, a loss of weight which is considerable in comparison with the earthy residue left when the combustible matter is burnt off.

	Loss on ignition.	Earthy matter.
Ticonderoga, N. Y.	3·85 per cent.	—
Ceylon II	2·56 „	1·28 per cent.
Borrowdale	3·8—5·08 „	7·0 „
Oberer Jenisei (Alibert)	2·53 „	4·5 „
Tunguska (Sidorow)	1·77—2·38 „	6·53 „

After fusion with caustic soda, digestion with acids, washing, and drying, inorganic matter is still left on combustion.

Ticonderoga	0·24 per cent.
Oberer Jenisei	0·60 „
Arendal	0·64 „

Some varieties of graphite burn on fused nitre, others do not. To the first class belong samples from Ceylon (I), Borrowdale, Oberer Jenisei, Upperniwik (Greenland), and Arendal; the volume-weight of these varies from 2·257 to 2 321. To the second class belong Ceylon (II), Ticonderoga, and graphite from blast-furnaces, in which the volume-weight varies from 2·17 to 2·30.

C. R. A. W.

The Greenstones. By THEODOR PETERSEN (J. pr. Chem. [2], vi, 197—227).

THE author divides the greenstones into two classes, viz.: (1.) The amphibolic or hornblende greenstones; (2.) The pyroxenic or augitic greenstones.

To the hornblende group belong diorite, with its varieties and congeners, the essential constituents of which are hornblende and a triclinic alkali-felspar. Sometimes also quartz is present, in which case the rock approximates to the trachytic series, and may even pass into syenite if it also contains orthoclase.

The augitic greenstones are the true basic rocks. They all contain a plagioclastic alkali or lime felspar, but no quartz. They may be conveniently divided into two groups, the older and the younger.

The older division, which is developed chiefly in the transition formation, includes the rocks of the diabase family, to which belong: (*a.*) True diabase. (*b.*) Melaphyr and augitic porphyry, which contain true augite, and are very much alike. (*c.*) Hypersthenite, containing ferruginous hypersthene, which, according to the recent investigations of Descloizeaux, crystallises in the rhombic system. (*d.*) Gabbro, containing comparatively light-coloured non-ferruginous enstatite, diallage, or smaragdite. All these rocks may be conveniently designated as "true greenstones."

To the later division of the augitic rocks belong those of the basaltic family: basalt, diorite, and basaltic lavas, for which, as proposed by Naumann, the collective name "trapp" may be retained.

The basic rocks, and especially those containing augite, exhibit on the whole a considerable resemblance to one another, and their percentage composition is also nearly the same. The alkaline silicates are more variously developed in the basaltic than in the diabasic rocks, which latter do not contain glassy felspar, nepheline, &c. In the former, on the other hand, the augitic substance has in the course of ages been more or less altered and converted into chlorite. Titaniferous magnetic iron ore (in some cases also titaniferous iron), and in small quantity apatite, are common to both groups.

Considerations on the Felspar Theory.—As the felspars are important constituents of greenstone, the author considers it necessary in the first place to discuss the theory of Tschermak respecting the constitution of these minerals. According to this theory (already explained in this Journal [2], x, 50, 288) the triclinic felspars are mixtures of the isomorphous minerals, albite and anorthite. Albite has the constitution, $Na_2Al_2Si_6O_{16}$, or, $\left.\begin{matrix}Na_2(Al_2)^{vi}\\Si_4\end{matrix}\right\}Si_4O_{16}$, and anorthite is $CaAl_2Si_2O_8$, or $(CaAl_2)_2Si_4O_{16}$; oligoclase, labradorite, and andesine are mixtures of these two species. This theory receives support from the facts that the proportion of alumina and lime in the triclinic felspars diminishes as that of silica increases, and that neither oliglocase free from lime, nor labradorite free from soda, has yet been discovered. Nevertheless the author has the following objections to this theory:—

1. Although oligoclase is essentially a soda-felspar, nevertheless the angles of well-defined oligoclase crystals from Vesuvius are much

nearer to those of anorthite than to those of albite.—2. The non-occurrence of perfectly pure varieties of felspar need not appear surprising when it is considered that the substance of felspar is easily decomposed, and almost always more or less altered.—3. If anorthite and albite are found crystallised together, orthoclase and albite ought to mix even more easily, which is not the case. Tschermak states that all orthoclases containing soda, and all albites containing potash, are mixed crystals. Now crystals of albite are found intergrown with those of orthoclase, and *vice versâ*, but transparent orthoclases rich in soda are perfectly homogeneous: they probably therefore contain soda as a necessary constituent.—4. The twin-striation peculiar to *plagioclastic* felspars is not always observed where we might expect it; orthoclase from the syenite of Laurvig in Norway, containing a large amount of soda, does not show it; neither does the plagioclase from the basalt of the Hartenberg in the Siebengebirge, though very rich in potash, exhibit any trace of admixture of orthoclase.—5. How does it happen that albite and anorthite occur in basic rocks by no means so frequently as oligoclase and labradorite?—6. Admitting the possible isomorphism of albite and anorthite, it is neverthess difficult to imagine the replacement of Si_2 by $CaAl_3$, or of Ca_2Al_2 by Na_2Si_2. Why should it be necessary to admit special laws of isomorphism in the case of the felspars when no such supposition is made in other cases of similar character? A well-defined transparent crystal of calcspar for example containing a considerable proportion of magnesium is still regarded as calcspar, and not as a mixture of calcspar and bitter spar. Garnet also, though sometimes richer in ferrous or manganous oxide, sometimes in lime or magnesia, nevertheless forms well-defined, transparent, homogeneous crystals, which can scarcely be regarded as mixtures. The same is the case with the hyalophane of Binnenthal, which has the composition $RO.Al_2O_3 . 4SiO_2$ ($R = \frac{1}{2}Ba + \frac{1}{2}K_2,Na_2$), and shows that a large proportion of potash renders felspars monoclinic. Lastly, there are numerous cases of artificially prepared crystals containing several isomorphous elements, which cannot easily be regarded as mixed crystals. Weltzien's experiments have shown how much copper can be introduced into rhombic zinc sulphate, $ZnSO_4 + 7H_2O$, or into monoclinic ferrous sulphate, $FeSO_4 + 7H_2O$, without altering the crystalline form or the amount of water. This could scarcely be the case if the crystals containing copper were mixtures. 7. Anorthite is easily and completely decomposed by strong hydrochloric acid, whereas oligoclase is scarcely attacked: hence, according to the mixture theory, hydrochloric acid might be expected to dissolve out the lime-constituent of calcio-sodic felspars more easily than the soda-constituent, but such is not the case.—8. Oligoclase from the diorite of Hof and from the diabases is free from lime; that from the gneiss of Aschaffenburg contains only a trace of lime. In all these oligoclases the oxygen-ratio of the alkalis, the alumina and the silica is as 1 : 3 : 10, whereas in albite and orthoclase it is as 1 : 3 : 12.

From these facts the author is disposed to regard Tschermak's theory as at least doubtful. He maintains that as numerous well characterised homogeneous orthoclases rich in soda or albites rich in potash must be regarded, not as mixtures but as individual bodies, the same must be

the case with oligoclase, and till the contrary is shown, also with labradorite. Andesine appears to be only an oligoclase rich in lime.

In all felspar analyses the following points must be borne in mind:—(1.) The presence of water indicates formation of kaolin, and therefore removal of alkalis. (2.) Iron oxides, magnesia, and frequently also lime, at least in part, must be regarded, not as essential constituents, but as due to admixtures of other silicates, especially augite and hornblende, or their products of decomposition.

The most important Constituents of the Basic Rocks.—It has long been questioned whether any triclinic felspar is a regular constituent of diabases. The author finds that oligoclase is usually present, whereas lime-felspar occurs in considerably smaller proportion, or is altogether wanting. In the younger greenstones, especially the basaltites, the oligoclase is sometimes replaced by orthoclase. Zeolites, mostly of comparatively recent formation, are diffused through all greenstones, especially the basaltites.

Augite and Hornblende.—The constitution of these minerals, and especially the part which alumina and ferric oxide play in them, has not yet been satisfactorily explained. Most of the analyses agree with the formula of a bisilicate, the excess of base which some of these exhibit being due to the iron which is often present as magnetic oxide. Augite and hornblende sometimes occur together in greenstones, the augite, however, generally predominating.

Chlorite.—The constitution of minerals of the chlorite family is but imperfectly understood, the obscurity arising chiefly from the fact that they are products of the more or less advanced transformation of augitic minerals, and therefore difficult to obtain pure. Their mean composition is best expressed by Rammelsberg's formula $2(3RO.SiO_2) + Al_2O_3.SiO_2 + 4H_2O$. In the diabases ferruginous chlorite is almost always present, the augite being sometimes completely converted into this mineral. It is often accompanied by a large quantity of finely divided magnetic iron ore.

Magnetic and Titaniferous Iron Ores.—Magnetic iron oxide is a regular constituent of the basic rocks, both old and new, especially of the augitic greenstones. It often contains titanic acid. Titaniferous iron is of frequent occurrence in the dolerites. Titanic acid occurs in basic rocks, sometimes isolated, more frequently, however, as titaniferous iron.

Apatite to the amount of several units per cent. is rarely absent from basic rocks, and is frequently met with in other rocks of plutonic origin, especially trachytes and lavas.

Formation of Serpentine.—Greenstones are not unfrequently serpentinised. Serpentine more or less distinctly stratified is often found amongst crystalline rocks, as gneiss, granite, diorite, gabbro, diabase, &c., but also nearest to those which contain a considerable quantity of magnesia. Silica and magnesia appear therefore to have a peculiar tendency to unite into a mass exhibiting the character of serpentine.

The Greenstones as Matrices of useful Minerals and Ores.—The beds of ore of Wittichen in Baden, appear to owe their existence to neighbouring hornblende slates containing nickel, cobalt, arsenic, bismuth, and silver. Many iron and copper ores, particularly the copper schist of Oberhessen, and the nickel and copper ores of the Dillenburg district, are probably

derived from diabase. The origin of the important deposits of phosphorite in Nassau must also be assigned to diabase, which is everywhere rich in apatite.

Method of Analysis.—The author's method of analysing the greenstones differs in nothing from the usual process, with exception of the determination of the ferrous oxide. This he accomplishes by decomposing the silicate in a flask made of glass free from iron, in an atmosphere of carbonic anhydride, with hydrofluoric and sulphuric acids. The iron is then titrated as usual.

W. R.

Diabase. By R. Senfter (J. pr. Chem. [2], vi, 227—256).

Diabase is a compact mixture of oligoclase, labradorite, and augite, usually also finely divided chlorite. Quartz is entirely, and mica almost entirely absent. Felspar is the chief constituent, and has a white or greyish white colour. Augite is present next in proportion, and has a greenish or blackish-brown colour. Chlorite is found in least quantity, and usually the more finely-grained the diabase, the greater is the quantity of chlorine present. Titanic iron ore and apatite are also constant constituents. Calcium carbonate, olivine, hornblende, and a few zeolites are sometimes found. It forms beds, dykes and veins in the palæozoic formations, and occurs in Nassau, in the Hartz, Westphalia, Devonshire, and Norway. It has a sp. gr. of 2·8—3·1, and begins to turn yellow on being heated to 200°. The diabase rocks are usually considered to be volcanic.

The following varieties have been distinguished by Petersen: 1. Fine-grained diabase; 2. Coarse-grained, resembling granite in appearance; 3. Porphyritic, containing crystals of labradorite, oligoclase and augite; 4. Compact, containing chlorite; and 5. Slaty diabase, also containing large quantities of chlorite. They are all of a greyish or blackish-green colour. The diabase from Nassau (X, XI, XII, of the following table) is found in calcareous deposits containing *stringocephali*.

The author gives a detailed account of a number of diabases analysed by him, which he summarises in a table, together with a number already analysed by others.

	I Stransko, Bohemia Tschermak	II Kiockersdorf Mahren. Tschermak	III Staufenberg Hartz Schilling	IV Hohgeiss Hartz Schilling	V. Laddekenburg Hartz Schilling
Specific gravity	2 859	2 953	3 003	2 95	2 802
SiO_2 ...	51 73	45 26	45 80	45 20	46 60
TiO_2	—	—	trace	—	—
Al_2O_3 ...	15 ·30	16 02	18 49	13 90	21 60
Fe_2O_3	10 56	7 29	5 67	9 40	2 86
FeO	3 ·38	7 09	4 90	4 ·92	6 40
MgO	3 ·20	6 40	5 ·74	7 80	6 48
CaO......	6 61	8 11	12 70	12 44	9 25
Na_2O	2 ·14	4 04	3 ·20	2 94	3 20
K_2O	1 37	0 33	0 60	0 40	0 94
H_2O......	4 ·85	3 60	3 24	3 16	3 ·10
P_2O_5	—	—	—	—	—
CO_2......	—	0 59	—	—	0 45
SO_3......	—	—	—	—	—
S	—	—	—	—	—
	99 14	98 73	100 34	100 16	100 ·88

	VI. Near Magdesprung Hartz. Carmichael.	VII. Near Magdesprung Hartz Keibel	VIII. Rosstrappe Hartz Fuchs	IX Near Allrode, Hartz Kayser.
Specific gravity	3 031	2 994	—	3 081
SiO_2..........	47 ·17	48 86	46 26	47 36
TiO_2	—	—	—	0 51
Al_2O_3	17 70	15 17	19 20	16 79
Fe_2O_3	4 ·07	3 ·32	10 06	1 53
FeO..........	5 81	6 71	10 ·20	7 93
MnO.........	0 57	0 35	—	0 44
MgO	5 59	7 56	5 52	6 ·53
CaO	14 ·10	11 34	9 17	10 08
Na_2O	2 42	3 ·11	0 53	2 85
K_2O	0 ·33	1 65	0 21	0 84
H_2O..........	3 71	2 46	0 53	3 ·05
P_2O_5	—	—	—	0 26
CO_2..........	—	—	—	0 48
SO_3..........	—	—	—	—
S	—	—	—	—
FeS_2	—	—	—	1 96
	101 ·07	100 ·53	101 ·68	100 61

	X. Odersbach Road, near Weilburg, Nassau. Senfter.	XI. Lahn Tunnel, near Weilburg, Nassau. Senfter.	XII. Gräveneck, near Weilburg, Nassau. Senfter.	XIII. Kupferberg, Oberfranken, Bavaria. Senfter.	XIV. Ribeira de Macanpes, Madeira. Senfter.
Specific gravity	2·848	2·918	2·995	2·969	2·79
SiO_2	46·04	48·62	41·17	45·03	49·15
TiO_2	1·46	1·86	3·08	0·33	0·83
Al_2O_3	17·35	16·25	13·24	17·59	17·86
Fe_2O_3	1·21	3·42	3·56	3·92	1·07
FeO	10·59	9·12	12·50	7·80	10·77
MnO }	0·41	trace	trace	trace	0·75
CoO }		trace	trace	trace	—
NiO }		trace	trace	—	trace
MgO	6·41	4·93	8·21	6·13	3·24
CaO	5·56	5·91	10·24	10·66	6·57
Na_2O	3·75	5·23	2·57	3·81	5·49
K_2O	2·11	1·60	1·60	1·41	2·29
H_2O	3·70	3·36	3·21	3·39	1·21
P_2O_5	0·64	0·36	0·53	0·33	0·99
CO_2	0·35	0·13	0·64	0·50	trace
SO_3	trace	trace	trace	—	—
S	0·09	trace	0·09	0·12	trace
FeS_2	—	—	—	—	trace
	99·67	100·79	100·64	101·02	100·22

Zinc, copper, and lead are found in traces in some of these specimens, as also chlorine, fluorine, arsenic, and organic matter.

As oligoclase and augite are hardly acted on by concentrated hydrochloric acid, even after long digestion, these minerals may be expected to be present in the residue unattacked by this acid. In the insoluble portion of the rocks which the author has analysed, the amount of lime is equal to that of the ferrous oxide and magnesia. This is characteristic of augite, and demonstrates its presence. On deducting the quantity of lime, ferrous oxide and magnesia necessary for augite, the residue agrees pretty well with the composition of oligoclase. The small quantity of carbonic acid present indicates calcspar, and the phosphoric acid points to the presence of apatite. The soluble portion consists mainly of chlorite and titanic iron ore.

The diabases contain as a constant constituent a triclinic alkaline felspar, which the author believes to be oligoclase; besides a lime felspar, probably labradorite. Augite is present next in amount; chlorite containing ferrous oxide and magnesia, apatite and titanic iron ore, and a little calcite, are always present. Ores are sometimes met with in small quantity, and owe their presence to the beds of rock in which diabase occurs. Many rocks commonly called hyperite belong to the family of diabases.

W. R.

Remarks on the Minerals Enclosed in Volcanic Rocks.

By F. SANDBERGER (Ber. der K. b. Academy, 1872, 172—176).

THE basalt rock of the Schlossberg, near Schwarzenfels, in the Hanauer Oberland and the Vorrderrhoen, contains in its upper very porous layer of a light greyish blue colour, fragments of perfectly white, fritted red sandstone, olivine, olivine gabbro and gneiss, with its mica completely fused to a black glass. The fragments of the same minerals which are found in the tufa surrounding the basalt have not undergone the same change; and the enclosed pieces of sandstone are in structure and composition exactly identical with the red sandstone found in the neighbourhood.

The fragments of olivine, some of which have a diameter of 0·5 meter, are covered with a very thin crust of slag, and show no trace of fusion in their interior; the mica of the gneiss is completely preserved. The tufa also contains pieces of red clay slate and chalk, neither of which occurs in the basalt-rock itself.

Similar cases are frequently met with in the dolerite.

It appears from this, that the tufa contains many fragments which were torn off by the highly compressed gases in the deeper parts of the eruption channel, and were ejected before the lava-stream itself filled the fissure.

Those minerals carried up by the lava being exposed for a longer period to the chemical action of the silicates and to a high temperature, were considerably metamorphosed; and those of a more acid character than the lava itself, were completely dissolved, whilst the more basic olivine, being better capable of resisting the chemical action, was preserved in cases where the gneiss, red sandstone, and other acid rocks, were dissolved in the basaltic magma.

The author thinks that the enclosures in the tufa are of greater value for the recognition of the rocks broken through, than the fragments enclosed in the basalt-rock itself, which, without comparison with the former, have frequently given rise to erroneous conclusions.

R. S.

South African Fibrous Quartz, a Pseudomorph of Crocidolite.

By F. WIBEL (Deut. Chem. Ges. Ber., vi, 185).

THIS was examined by Klaproth in 1815, but his analyses, according to the author, are incomplete and incorrect. A full account of the author's examination will appear in Leonhard and Geinitz's *Neues Jahrbuch für Mineralogie*. A brief statement of his results only is given in this paper.

A. *Brown Fibrous Quartz.*

Specific gravity at 15° C = 3·05.

Silica	57·46	or	Silica	57·46
Ferric oxide	37·56		Göthite, Fe_2O_3,H_2O	41·79
Water............	5·15		Water............	·92
	100·17			100·17

Strong acids dissolve out all the $Fe_2O_3.H_2O$ as colouring matter, and leave a pure white quartz of magnificent satiny lustre, and in parallel fibres.

B. *Blue Fibrous Quartz.*

Specific gravity at 15° = 2·69.

Silica	97·27	or nearly	Quartz	96·5
Ferrous oxide	1·67		Crocidolite	2·5
Lime	0·15		Hydrated oxide of iron, &c.	1·0
Sodium oxide	0·15			
Water	0·76			
	100·00			100·0

Apart from the hydrated oxide of iron, which is distinctly visible, this blue mineral is, without doubt, a mixture of fibrous quartz and crocidolite, although a separation of the two cannot be effected, in consequence of the difficult solubility of the latter in acids.

Both species are evidently pseudomorphs of crocidolite by conversion. In the brown variety, this conversion is complete, and all the ferrous oxide has become ferric oxide; while, in the blue variety, some crocidolite remains. A case is here afforded of a compound silicate suffering complete decomposition into pure silica, without thereby changing its form or structure.

E. D.

Pseudomorphs of Gypsum and Glass in the form of Gooseberries. By F. Wibel (Deut. Chem. Ges. Ber., vi, 183).

The author has examined some concretions which had formed in a glass of preserved green gooseberries, and appeared to have been true pseudomorphs of the substance of the gooseberries. The vessel, which was of soda-lime glass, was much corroded in contact with the preserve.

The concretions were partly globular shells, partly casts of the conical ends of the gooseberry stalks. They had a foliate-radiate structure, and a beautiful satiny lustre on the surface. These appearances were due to minute particles of glass which were cemented together by granular gypsum. On treatment with water, the glass was at once set free, and crystalline masses of gypsum formed. A little organic matter, apparently albuminoid and colouring, was present; nearly 33 per cent. of glass and 57 of gypsum ($CaSO_4 + 2H_2O$).

The author attributes the corrosion and disintegration of the glass to the action of the malic acid in the gooseberries, by which soluble silicates and malates were produced; and the formation of the gypsum to the action of the sulphates of the gooseberries upon the calcium of the glass.

E. D.

Amount of Oxygen Dissolved in Rain and in River-water. By A. Gerardin (Compt. rend., lxxv, 1713—1714).

Thirteen determinations of oxygen in rain were made between November 25 and January 8, by the method described at page 88 of this

volume, the extremes, in c.c. per litre, being 2·59 and 4·80, and the mean, 3·74. On October 29, it appears to have been exceptionally high, viz., 8 00 c.c. per litre. Fine and long-continued rain contained less oxygen than rain which was heavy and of short duration. The author thinks that the greater division in the first case causes a loss of oxygen.

The oxygen in the water of the Seine was determined eight times between October 9 and January 8, the extremes in c.c. per litre being 3·33 and 3·99, the mean being 3·65. On October 30, it was much more in amount than this, being 6·00 c.c. per litre.

B. J. G.

On some Mineral Waters containing Iron.

By E. REICHARDT (Arch. Pharm. [3], ii, 124—130).

CONTAINS the results of analyses of the mineral waters of (1) Lobenstein, near Ebersdorf; (2) Liebenstein in Thuringia; and (3) Steben in Bavarian Upper Franconia, together with geological details of the districts in which the springs are respectively situate.

J. R.

On some Mineral Springs of Java, containing Iodine.

By E. REICHARDT (Arch. Pharm. [3], ii, 130—137).

CONTAINS a detailed account of several springs in Java, which, from the relatively large amounts of iodine they contain, the author thinks will sooner or later be employed as sources of that element, though, possibly owing to unfavourable local circumstances, they have hitherto not been so utilised.

The following is the result of an analysis, made by the author, of the water of the Genock Watoe spring:—100 grams contained

	grams.		grams.
KCl	0·0303	$CaSO_4$	0 0036
NaCl	2·3006	$CaO.2CO_2$	0·0687
NaI	0·0138	Na_2SiO_3	0 0058
$Na_2O.2CO_2$	0·1720	NH_4NO_3	0 0050
$MgCl_2$	0·0334	$(NH_4)_2O.2CO_2$	0·0306

J. R.

Analyses of some Waters of the Island of Cephalonia.

By F. WIBEL (Deut. Chem. Ges. Ber., vi, 184).

THIS paper contains a number of analyses of the sea-water and other waters near the peninsula of Argostoli in Cephalonia. These analyses were undertaken, in connection with other researches, to throw light upon the remarkable "sea mills" (Meermuehlen) of Argostoli.

It has been supposed that in these "sea mills," a simple influx of sea-water into the soil takes place; but these analyses show that the water is always brackish, consisting of 7 parts fresh water and 4 parts sea-water.

E. D.

Analysis of the Stahlbrunnen at Homburg. By R. FRESENIUS (J. pr. Chem. [2], vii, 20—26).

THIS well is bored to the depth of 199 feet, the bore being 10 inches wide. The water flows at the rate of 90 litres per hour, the amount of gas evolved in the same time being 12 litres; the proportion between these is therefore as 7·5 : 1. The temperature of the water was 18 75, that of the air being 11°. Specific gravity at 20° = 1·00708.

On standing in the air, an ochreous deposit of ferric oxide is thrown down. The gas spontaneously evolved from the water consists of—

Carbon oxide	87·57 vols. per 100
Nitrogen	12 07 „ „
Light hydrocarbons	0 36 „ „
Sulphuretted hydrogen	traces.

A quantitative analysis gave the following results:—

	In 1,000 parts.			
Sodium chloride	5·863199			
Potassium „	·248320			
Lithium „	·012067			
Ammonium „	·013187			
Calcium „	·497721			
Magnesium „	·315457			
„ iodide	·000015			
„ bromide ..	·000676			
Potassium nitrate	·001874			
Calcium sulphate	·003725			
Strontium „	·010616			
Barium „	·000420			
Calcium carbonate....	·722479	=	Calcium bicarbonate..	1·040370
Magnesium „	·061417	=	Magnesium „ ..	·093588
Ferrous „	·071385	=	Ferrous „ ..	·098463
Manganous „	·004054	=	Manganous „ ..	·005605
Nickel and cobalt carbonate	·000024	=	Nickel and cobalt bicarbonate....	·000932
Calcium phosphate ..	·001017			
Silica	·017190			
	7·844843	=	Total solids.	

Carbon dioxide combined with the carbonates to form—

Bicarbonates................	0 378699
Free carbon dioxide..........	2 042990
Sulphuretted hydrogen	0·000671
	10·267203 = total solid and gaseous constituents.

The water also contains minute traces of cæsium, rubidium, aluminium, copper, and antimony oxides; arsenic and boric acids, fluorine and organic matter.

M. M. P. M.

Sulphur Springs at Lostorf in the Solothurn Jura. By Dr. G. Briegel (N. Repert. Pharm., xxii, 75).

The water from two wells, A and B, was examined with the following results in grams per litre:—

Well A.

Potassium sulphate	0·6714	Calcium carbonate	0·3425
Sodium chloride	3·0200	Potassium thiosulphate.	0·0734
Magnesium carbonate ..	0·2048	Potassium sulphide	0·3284
Alumina and trace of phosphoric acid....	0·0130	Ferrous carbonate......	0·0087
Silica	0·0226		4·6848

Half-combined carbonic acid 0 1310
or 66·05 c.c. at 0° and 760 mm.

Half-combined sulphuretted hydrogen.... 0 0911
or 59 8 c.c. at 0° and 760 mm.

Well B.

Chlorine..............	1·4270	Sodium chloride	2·3515
Carbonic acid	0 3620	Calcium carbonate	0·8236
Sulphuretted hydrogen..	0·1585	Sulphur	0·1492

Both waters were turbid, and deposited sulphur on long exposure to the air; they had an alkaline reaction both at first and after boiling (whereby a yellow colour was produced).

C. R. A. W.

Organic Chemistry.

Synthesis of Circularly Polarising Organic Bodies—Construction of Dextro- and Lævo-Tartaric Acids from Ethylene. By E. Jungfleisch (Compt. rend., lxxvi, 286—290).

It has been doubted whether it is possible, by mere chemical construction or synthesis, without the intervention of living organism, to produce compounds endued with the power of rotatory polarisation of light. Perkin and Duppa showed in 1860 how to transform succinic acid into tartaric acid. The acid which they obtained was studied by Pasteur, and found to consist of racemic acid and inactive tartaric acid. But their researches did not throw any light on this particular question. The succinic acid they employed was the ordinary natural product; and, as Pasteur remarks, the question arises whether this succinic acid is inactive in its nature, or inactive *by compensation*—a kind of inactivity which Pasteur himself has shown how to obtain in the case of the tartaric acids—or whether natural succinic acid may not even be an active body of very feeble power.

Maxwell Simpson has obtained succinic acid, starting from olefiant

gas; and the author of the present paper, having given a method for the conversion on a large scale of inactive tartaric acid into racemic acid, has now succeeded in forming the active acids from olefiant gas as a starting point.

The complete operation, as there is in each of the stages considerable loss, required a large quantity of material, and M. Jungfleisch has modified the processes formerly employed so as to obtain a much better yield. Commencing with as much as 3,800 grams of ethylene dibromide, he obtained by Simpson's method 300 grams of ethylene dicyanide. This was then converted into succinic acid in the following way:—The coloured dicyanide obtained as a residue from the distillation of the alcoholic solution from which the bromine had been removed as potassium bromide, was mixed with 5 or 6 times its volume of water and heated on a water-bath. Little by little nitric acid diluted with an equal weight of water was then added; and succinic acid was obtained by the following reaction:—

$$C_2H_4(CN)_2 + 2HNO_3 + 4H_2O = C_4H_6O_4 + 2(H_4N.NO_3).$$

The liquid was neutralised with potash, and the succinic acid precipitated by a lead salt. Finally the succinic acid was obtained by precipitating the lead with sulphuretted hydrogen.

In this way 300 grams of pure crystallised succinic acid was obtained.

From this, by the processes of Perkin and Duppa, and of Kekulé, somewhat modified so as to give a better yield, 62 grams of crystallised calcium tartrate was obtained from 247 grams of succinic acid.

The calcium tartrate proved to be a mixture of calcium racemate and inactive calcium tartrate; and it answered in all respects to the calcium tartrate obtained from natural succinic acid. The whole of the calcium salt was then freed from its metallic part, and by the process of the author already referred to, the whole of the inactive tartaric acid was turned into racemic acid.

Lastly, by Pasteur's process the racemic acid was broken up. The double tartrate of sodium and ammonium having been formed and crystallised, the hemihedral crystals, right-handed and left-handed, were obtained, and on being dissolved and subjected to the polariscope, they exhibited perfectly the property of right-handed and left-handed polarisation. The solution did not display rotatory power quite so intense as that which theory would expect, but very nearly so, and, considering that the experiments were made with the results of the first crystallisation, they were perfectly satisfactory. Without any doubt they show that these organic compounds may be constructed to give rotatory polarisation by processes belonging purely to the laboratory.

J. T. B.

Note on the Synthesis of Marsh Gas and Formic Acid, and on the Electric Decomposition of Carbon Oxide. By Sir B. C. Brodie (Proc. Roy. Soc., xxi, 245—247).

On submitting hydrogen and carbon oxide to the action of electricity in the induction tube, a contraction of the mixed gases was observed,

and after the fifth hour, on analysis, they were found to contain about 6 per cent. of marsh-gas, which had thus been synthetically produced; the result of the reaction being expressed by the equation—

$$CO + 3H_2 = CH_4 + H_2O.$$

In a similar experiment, made with a mixture of hydrogen and carbon dioxide, the resultant gas was found to contain carbon oxide, and at the same time minute drops of an oily liquid appeared in the tube. These, on examination, were found to give the characteristic reactions of formic acid—

$$H_2 + CO_2 = H_2CO_2.$$

When pure and dry carbon oxide is circulated through the induction tube, and then submitted to the action of electricity, a decomposition of the gas occurs, attended with a gradual and regular contraction, carbonic oxide being formed, whilst a transparent film of a reddish-brown colour is deposited on the sides of the tube. It is entirely soluble in water, and yields a coloured solution possessing an intensely acid reaction. This solid deposit is an oxide of carbon, but in different experiments does not present the same composition. The author has, however, succeeded in identifying two of these "oxycarbons," namely, C_4O_3, and C_5O_4, which may be regarded as corresponding to crotonylene, C_4H_6, and valerylene, C_5H_8, in the analogous hydrocarbon system of which acetylene is the first term.

C. E. G.

Trichloracetic Acid and its Salts. By A. Clermont (Compt. rend., lxxvi, 774).

The author has obtained trichloracetic acid by adding a concentrated solution of chromic acid, in small portions at a time, to a strong solution of chloral hydrate, the whole being kept cool He has also prepared the following trichloracetates. *Mercurous trichloracetate*, $C_2Cl_3O_2Hg$, is prepared by mixing concentrated solutions of mercurous nitrate and neutral potassium trichloracetate. It is difficultly soluble in water. *Mercuric trichloracetate*, $(C_2Cl_3O_2)_2Hg$, is obtained in prismatic needles, when precipitated mercuric oxide is dissolved in trichloracetic acid. It is slightly soluble in water, and rather more soluble in alcohol and ether. It does not decompose as the corresponding acetate does. When zinc carbonate is dissolved in a weak solution of the acid, *zinc trichloracetate*, $(C_2Cl_3O_2)_2Zn + 6\,aq.$, is produced. After standing for several months over quicklime, it appears in the form of brilliant, micaceous, very deliquescent spangles. When alcoholic solutions of trichloracetic acid and urea are mixed together, fragile plates of *urea trichloracetate*, $COH_4N_2.C_2Cl_3O(OH)$, are produced.

B. J. G.

The Chloride, Bromide, and Iodide of Trichloracetyl. By H. Gal (Compt. rend., lxxvi, 1019—1021).

Phosphorus trichloride acts readily upon trichloracetic acid, and a product is obtained, which, after rectification, boils regularly at 118°.

Analysis proved it to be *trichloracetyl chloride*, $C_2Cl_3O.Cl$. Phosphorus pentachloride reacts in a similar manner, but the trichloride is more advantageously employed, inasmuch as it is difficult to separate the resulting oxychloride. Trichloracetyl chloride, when treated with water, forms trichloracetic acid and hydrochloric acid; with alcohol it yields ethyl trichloracetate. The action of phosphorus tribromide upon trichloracetic acid produces *trichloracetyl bromide*, $C_2Cl_3O.Br$, a liquid boiling at *about* 143°. The reactions of the bromide are precisely analogous to those of the foregoing chloride.

Trichloracetyl iodide is more difficult to prepare. A small quantity of a liquid was obtained, boiling at about 180°, which decomposed when treated with water and with alcohol; but its composition was not satisfactorily made out.

J. W.

Derivatives of the Silicium Oxychlorides. By L. TROOST and P. HAUTEFEUILLE (Compt. rend., lxxv, 1710—1712).

THE various silicic oxychlorides which the authors have already shown to be obtainable by submitting one of the series to different degrees of heat, react with absolute alcohol in a similar way to that in whic Ebelmen found that silicium tetrachloride, $SiCl_4$, does. The whole of the chlorine is evolved as hydrochloric acid, and a silicic ether is formed containing the same number of molecules of ethoxyl, OC_2H_5, as there were atoms of chlorine in the oxychloride. Thus, just as silicium tetrachloride produces the tetrethyl-silicic ether, $Si(OC_2H_5)_4$, so the oxychloride, $Si_2\left\{\begin{matrix}O\\Cl_6\end{matrix}\right.$, yields, as Friedel and Ladenburg have shown, the hexethyl-disilicic ether $(Si_2O)^{vi}(OC_2H_5)_6$. The analogous derivative from the oxychloride, $Si_4\left\{\begin{matrix}O_4\\Cl_8\end{matrix}\right.$, has now been obtained; it has the formula $(SiO)''_4(OC_2H_5)_8$, or *octethyl-tetrasilicic ether*. To obtain this substance in a state of purity, it is necessary to eliminate as soon as possible the hydrochloric acid formed in the reaction, otherwise a number of other ethers are also produced. Absolute alcohol is therefore allowed to fall drop by drop into a tubulated retort containing the oxychloride, which is kept near its boiling point. The acid is thus removed as soon as it is formed, and the retort at the end of the operation contains the almost perfectly pure ether, which is a mobile liquid of sp. gr. 1·071 at 0°, 1·054 at 14·7°; vapour density, 19·54; very soluble in ether and in alcohol; insoluble in water, and when mixed with it remaining in the form of oily drops, which gradually become opalescent, then white, and finally split up into silica and alcohol.*

By the action of ammonia on the ether a result was obtained similar

* It would seem simpler to formulate the oxychloride thus, $Si\left\{\begin{matrix}O\\Cl_2\end{matrix}\right.$, and the ether thus, $(SiO)''(OC_2H_5)_2$, which is the formula of the diethyl-silicic ether described by Ebelmen (*Ann. Chim. Phys.* [3], xvi, 141), with which it appears to be identical, the specific gravity of Ebelmen's compound being 1·079, its reaction with water the same as that which takes place with this ether, and its boiling point being 350°. The boiling point of the author's ether is not given, but it is stated that its vapour-density was determined at the boiling point of mercury, or 350°.—B. J. G.

to that of Dumas, who obtained oxamethane by acting on neutral ethyl oxalate with this gas. When ammonia is passed into an ethereal solution of the silicic ether, an oily liquid is obtained, having the formula $(SiO)_4 \left\{ \begin{matrix} (OC_2H_5)_7 \\ NH_2 \end{matrix} \right.$. By prolonging the action, a second atom of amidogen is introduced, the resulting compound being, however, very unstable. Hexethyl-disilicic ether, $Si_2O(OC_2H_5)_6$, behaves in a similar way, forming a rather stable oil, $Si_2O \left\{ \begin{matrix} (OC_2H_5)_5 \\ NH_2 \end{matrix} \right.$, and a more easily decomposible body containing two atoms of amidogen. These amido-derivatives may also be obtained, though less easily, by acting with ammonia on the corresponding oxychlorides dissolved in anhydrous ether.

B. J. G.

Solution of Ethylene in Sulphuric Acid.

By Buttlerow and Gorgainow (Deut. Chem. Ges. Ber., vi, 196).

Strong sulphuric acid at 160°—170° perfectly absorbs ethylene. In Berthelot's well-known experiment the absorption may be due to the heat developed by friction.

C. R. A. W.

Preparation of Sulpho-butyric Acid.

By Hemilian (Deut. Chem. Ges. Ber., vi, 196).

Sulphuric monochlorhydrin, $SO_2 \left\{ \begin{matrix} Cl \\ OH \end{matrix} \right.$, acts on butyric acid at 148°, forming *sulphobutyric acid*, an uncrystallisable syrup, furnishing crystalline salts insoluble in alcohol, the calcium salt excepted.

C. R. A. W.

Isocrotyl Ether.

By Anna Wolkow (Deut. Chem. Ges. Ber., vi, 196).

Sulphuric acid of the strength of 1 per cent. acts at 150°—160° in sealed tubes on isocrotyl ether, producing a quantity of acetone larger than that which corresponds with the isocrotyl group.

C. R. A. W.

Neutral Compounds derived from Mannite.

By G. Bouchardat (Bull. Soc. Chim. [2], xix, 199—204).

This paper is an extension of the one already abstracted (p. 160 of this volume), and contains the following additional information.

Dichloromannite.—Ten hours is here stated to be the time required for the production of this substance. It is soluble in 22 parts of water at 14°. Its solutions deviate the plane of polarisation to the left, its rotatory power being $[\alpha]_y = -3{\cdot}9°$ to $-3{\cdot}5°$. (These observations were made for the *yellow* ray, and not, as is usually the case, for the purple-blue or the red ray.)

Dichlorotetranitromannite melts at 145°.

Monochloromannitan.—After boiling dichloromannite with water, and concentrating, the solution is exactly neutralised with potassium carbonate, and then agitated with ether. The ethereal solution when evaporated to dryness yields monochloro-mannitan. Its rotatory power is very similar to that of mannitan, viz., $[\alpha]_y = 6{\cdot}99°$. Heated in a sealed tube with a saturated solution of hydrobromic acid, it is converted into a crystalline substance slightly soluble in cold water, which is probably bromochloro-mannite. With hydrochloric acid under the same conditions it is reconverted into dichloro mannite. Cold nitrosulphuric acid converts it into a nitrochlorinated body insoluble in water, but soluble in ether and alcohol.

Dibromomannite.—The crystallisation of this compound, which often takes several months, may be brought about more quickly by evaporating rapidly in the cold a few drops of the solution with hydrobromic acid, and adding the traces of crystalline matter thus obtained to the contents of the tube diluted with their own bulk of water. *Dibromotetranitromannite* melts at 14°. *Monobromomannitan* is soluble, in all proportions, in water. All the soluble ethers derived from mannite have a rotatory power, generally to the right. Loir and the author have proved that mannite has no such power. Mannitan, however, has a dextro rotatory power of 6·5°.

B. J G.

On Pure Gallotannic Acid. By J. Löwe (Zeitschr. Anal. Chem., xi, 365—381).

After noticing the views that have from time to time been put forward by other chemists as to the constitution of gallotannic acid, the author describes an experiment undertaken for the purpose of ascertaining whether tannic acid under the influence of dilute acids is capable of splitting into gallic acid and glucose.

120 grams of tannic acid heated with 2 per cent. sulphuric acid for eight days gave, in addition to gallic and unchanged tannic acid, no more than about 1·5 gram of yellowish-brown amorphous substance, which, however, the author does not consider to be glucose.

The author describes in detail the processes he adopted for the purpose of obtaining pure gallotannic acid.

1. *By Dialysis.*—Tannin, obtained by precipitating the concentrated aqueous solution with ether, was dissolved in alcohol of 90 per cent. and allowed to diffuse through a porous diaphragm into alcohol of the same strength. The products obtained at intervals of eight days were dried, first *in vacuo*, then at 120° and analysed. Three series of analyses were thus made with the following mean results:—

	I.	II.	III.
C....	51·499	51·569	51·542
H....	3·748	3·730	3·734

2. *By Ether.*—The best commercial tannin dried by long exposure over sulphuric acid was shaken up with several successive portions of dry ether. The dissolved tannin after drying at 120°, presented the

same characters as the tannin purified by dialysis, and gave the same analytical results. Three series of analyses were made—

Mean.	I.	II.	III.
C....	51·580	51·618	51·680
H....	3·674	3·726	3·657

3. *By means of Common Salt and Acetic Ether.*—When tannin was shaken up with a solution of common salt, consisting of equal volumes of saturated salt-solution and water, nearly the whole of it dissolved. The clear liquid was then saturated with pure salt and set aside. A viscid mass of tannin was deposited, which was redissolved and again precipitated by the addition of salt. The amorphous deposit was then redissolved in dilute salt-solution and extracted by shaking with acetic ether. The tannin thus purified was dried at 120° previous to analysis. It gave, as the mean of three analyses, C = 51·600, H = 3·661 per cent.

The foregoing numbers agree with those obtained in the old analyses of Berzelius and Mulder, and are in accordance with the formula $C_{14}H_{12}O_{9}$. If this formula is accepted, gallic acid must be a product of oxidation. The author, however, finds that by the action of dilute acids alone, in the absence of air or oxygen, pure tannic acid is wholly converted into gallic acid. Recollecting, therefore, the opinion of Mulder that tannic acid, even when dried at 120°, retains water, some experiments were made for the purpose of ascertaining whether, on heating tannic acid which had been exposed to this temperature to a higher temperature, any loss is sustained, and whether this loss is constant and due solely to volatilisation of water.

The result was, that by heating to 140°—145°, a loss amounting to 0·8 per cent. was observed, and the dry residue submitted to analysis gave, as the mean of the first series, C = 52·126, H = 3·336. Three analyses of another specimen furnished as a mean C = 52·073, H = 3·248. These results support the formula $C_{14}H_{10}O_{9}$ originally given by Mulder, which requires C = 52·174 H = 3·106.

Notwithstanding that he regards this formula as established, the author does not consider the transformation of tannic into gallic acid as resulting simply from the assimilation of water.

The relation of tannic to gallic acid is therefore still obscure.

W. A. T.

Diphenyl. By C. Latschinoff (Deut. Chem. Ges. Ber., vi, 193).

Phenyl chloride was used instead of bromide, as starting point in the preparation of diphenyl. According to Fittig's process, copper did not act on either; the yield was much below the theoretical amount.

The mono- and di-sulphodiphenylic acids were separated by means of the copper salts: the mono-acid gives a potassium salt, $C_{12}H_{9}SO_{3}K + 2H_{2}O$, moderately soluble in water, readily in dilute alcohol; when melted with caustic potash, this salt forms *oxydiphenyl*, $C_{12}H_{9}.OH$, readily soluble in 40 per cent. alcohol, ether, and caustic potash-solution. This body gives no coloration with ferric chloride, and is not attacked by ammoniacal solution of silver nitrate even when boiling.

Lead acetate gives a precipitate insoluble in acetic acid; it melts at 164°—165°, boils at 305°—308°, and distils with water vapour, and sublimes unchanged: benzoyl chloride forms *benzoyl-oxydiphenyl*, $C_{12}H_9O.COC_6H_5$, melting at 152°, and difficultly soluble in alcohol and ether. When cautiously warmed with sulphuric acid, it forms mono- and di-sulpho-oxydiphenylic acids separable by means of their potassium salts, that of the latter being the most soluble. The mono-salts give no colour with ferric chloride, but the di-salts give a characteristic indigo colour.

The mono-potassium salt is $C_{12}H_8(KSO_3)(OH) + H_2O$; when distilled, it furnishes the di-salt and oxydiphenyl. The di-salt is $C_{12}H_7(KSO_3)_2.OH + 1\frac{1}{2}H_2O$. When fused with potash, it first forms mono-salt and then *diphenol*.

$$^{*}C_{12}H_8(KSO_3)_2 + KOH = K_2SO_3 + C_{12}H_8(KSO_3)(OH)$$
$$C_{12}H_8(KSO_3)_2 + 2KOH = 2K_2SO_3 + C_{12}H_8(OH)_2.$$

Nitric acid acts on oxydiphenyl, forming mono- and di-nitro-oxydiphenyl; the first is volatile with water vapour, the second not; they melt at 67° and 154° respectively.

C. R. A. W.

Phenanthrene and Anthracene. By R. Fittig (Deut. Chem. Ges. Ber., vi, 167—169).

Diphenylene ketone combines with fused caustic potash, forming the potassium salt of *phenyl-benzoic acid*, $C_6H_5.C_6H_4.CO_2H$; the free acid, which, as well as its salts, can easily be obtained quite pure, melts at 110°—111°. By heating its calcium-salt with quick lime, the ketone is regenerated, and only a small quantity of diphenyl is formed. This reaction appears at the first glance very remarkable; but it is quite in accordance with the formation of anthraquinone and its hydroxyl-derivatives from benzoic acid and oxybenzoic acids.—

$$\begin{matrix} C_6H_4H.CO.OH \\ C_6H_4H.CO.OH \end{matrix} = C_6H_4\begin{matrix} \diagup CO \diagdown \\ \diagdown CO \diagup \end{matrix}C_6H_4 + 2H_2O.$$

2 mol. of benzoic acid. Anthraquinone.

$$\begin{matrix} C_6H_4.CO.OH \\ | \\ C_6H_4H \end{matrix} = \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\!\!>CO + H_2O.$$

Phenyl-benzoic acid. Diphenylene ketone.

The only difference between the two reactions is, that for the formation of the quinone, two molecules of benzoic acid are required, while the ketone is produced from one molecule of phenyl-benzoic acid.

This seems also to be the reason why this reaction, which on heating calcium benzoate, is only a subordinate one, appears as the principal one in the case of phenyl-benzoic acid.

* This formula represents the disulpho-acid of diphenyl, not of oxydiphenyl.—C. R. A. W.

According to this view, anthraquinone is a double ketone, and does not contain two oxygen-atoms linked together, as assumed by Graebe, in his quinone theory; and this appears the more probable, as on fusing this quinone with potash, it splits up again into two molecules of benzoic acid, just as the ketone forms again one molecule of phenyl-benzoic acid. The formation of anthraquinone from anthracene is also easily explained:—

$$C_6H_4\left\langle\begin{matrix}CH\\ |\\ CH\end{matrix}\right\rangle C_6H_4 + O_3 = C_6H_4\left\langle\begin{matrix}CO\\ \\ CO\end{matrix}\right\rangle C_6H_4 + H_2O.$$

C. S.

On Phenols. By H. HUEBNER and O. BRENKEN (Deut. Chem. Ges. Ber., vi, 170—173).

BY dissolving bromine and phenol in glacial acetic acid, and gradually mixing the well-cooled solutions, *monobromophenol* is formed, which crystallises out when the liquid is surrounded by a powerful freezing mixture, while in the mother-liquor a liquid isomeride appears to be left behind. The same solid monobromophenol is obtained by distilling monobromosalicylic acid (formed by direct substitution) with quick-lime.

Monobromophenol is sparingly soluble in cold, more freely in hot water and readily in acetic acid, alcohol and chloroform, from which it is obtained in colourless crystals, often an inch long and resembling alum. It melts at 63°—64°, and boils at 235°—236°.

Nitrobromophenol, $C_6H_3(NO_2)BrOH$, is sparingly soluble in cold water and alcohol, and crystallises from boiling alcohol in long, brilliant sulphur-yellow needles melting at 87°—88°. $[C_6H_3(NO_2)BrO]_2Ba$ forms small red needles having a golden-green lustre, and crystallises from a very dilute alcoholic solution in large, rhombic, blood-red plates. $C_6H_3(NO_2)BrOK + 2H_2O$, crystallises in transparent blood-red needles, with a golden-green lustre. $C_6H_3(NO_2)BrONa$ forms small deep-red needles having the same lustre. This nitrobromophenol appears to be identical with that obtained by Brunck from nitrophenol and bromine.

Dinitrobromophenol, $C_6H_2(NO_2)_2BrOH$, is readily soluble in boiling alcohol, and forms long, slender, pale yellow needles, melting at 115°. $[C_6H_2(NO_2)_2BrO]_2Ba + 3\frac{1}{2}H_2O$ separates from a hot solution first in sulphur-yellow needles which after some time change into transparent, dark-yellow, rhombic prisms. On heating it to 150°, it loses its water and yields an amorphous, blood-red powder, which quickly takes up water and turns yellow again. $[C_6H_2(NO_2)BrO]_2Ca + 12H_2O$ forms small yellow silky needles, which in the air lose water and acquire a red colour. $C_6H_2(NO_2)BrOK + 1\frac{1}{2}H_2O$ crystallises from hot water in dark yellow silky needles, losing in the air half a molecule of water. This dinitrobromophenol appears to be identical with that obtained by Armstrong by the action of nitric acid on potassium dibromophenol-sulphonate, and that which Laurent prepared by dissolving dinitrophenol in warm bromine.

C. S.

Contributions to the History of the Orcins.—Amido Derivatives of Orcin. By J. STENHOUSE (Proc. Roy. Soc. xxi, 122—127).

Amido-diimido-orcin, $C_7H_5(NH_2)(NH)_2O_2$.—This base is produced by the oxidation of the triamido-orcin prepared by the action of reducing agents, such as sodium-amalgam, tin and hydrochloric acid, or zinc and an acid, on trinitro-orcin. The author prefers to treat trinitro-orcin, suspended in water, with sodium-amalgam in a closed vessel until the solution becomes colourless; then to oxidise the clear solution by agitating it with air until it assumes a brilliant blue colour; and finally to precipitate the amido-diimido-orcin thus formed as hydrochloride by the addition of an excess of strong hydrochloric acid. On treating the hydrochloride with a slight excess of dilute ammonia, it is decomposed, leaving the free base in an impure state This is dissolved in warm dilute acetic acid, filtered, and precipitated by a slight excess of ammonia. Two or three solutions and reprecipitations suffice to render it pure, when it forms small needles, having a deep green metallic lustre by reflected light. They are insoluble in most menstrua; a solution of sodium hydrate, however, dissolves them with a fine deep blue colour. As might be expected, treatment with sodium-amalgam reconverts them into triamido-orcin.

The *hydrochloride*, $C_6(CH_3)(NH_2)(NH)_2(OH)_2HCl$, crystallises, according to circumstances, either in long silky needles of a brownish-red colour, in rhomboidal plates, or in dark red thick prisms It is insoluble in alcohol and ether, moderately soluble in cold, and easily in boiling water, but is at the same time partially decomposed. The *sulphate*, $[C_6(CH_3)(NH_2)(NH)_2]_2SO_4 + H_2O$, forms minute lustrous plates, which are purple by reflected light, and much less soluble in water than the hydrochloride. The *nitrate* closely resembles the sulphate in appearance, but is much more soluble in water. The *oxalate* is obtained in very slightly soluble purple scales, and the *picrate* in iridescent green needles and plates, which are insoluble in alcohol and almost insoluble in water. The *acetate*, which is very soluble in cold water and does not crystallise well, is prepared by dissolving the free base in acetic acid. As the aqueous solutions of the amido-diimido-orcin salts are decomposed under the influence of heat, the author recommends to prepare them by adding the corresponding acid to a solution of the acetate.

Triamido-orcin.—On boiling trinitro-orcin with tin and hydrochloric acid until it becomes colourless, separating the tin by hydrosulphuric acid, and evaporating the solution in a vacuum, long colourless needles of triamido-orcin hydrochloride are obtained, but owing to their great solubility and the readiness with which they absorb water and deliquesce, the salt was not obtained in a state fit for analysis. On passing a current of sulphuretted hydrogen through a solution of ammonium sulphydrate in which amido-diimido-orcin is suspended, the latter rapidly loses its colour and becomes converted into a sandy deposit consisting of colourless crystals. These are apparently triamido-orcin, and on exposure to the air rapidly acquire a metallic green lustre and become converted into amido-diimido-orcin. They also dissolve in

hydrochloric acid, the solution acquiring a deep red colour and depositing crystals of amido-diimido-orcin hydrochloride when exposed to the air.

C. E. G.

Formation and Decomposition of Ketones. By W. STAEDEL (Deut. Chem. Ges. Ber., vi, 178—181).

FUSION of benzophenone-paradisulphonic acid with potassium hydrate (*Chem. Soc. J.* [2], x, 406) yields nearly the calculated quantities of paroxybenzoic acid and phenol. The author has applied this reaction to other ketonic bodies. Benzophenone yields almost the theoretical quantities of potassium benzoate and benzene.

Anthraquinone heated with potassium hydrate and water yields an acid which appears to be different from benzoic acid. The author hopes to be soon able to say whether this acid is Zincke's benzoylbenzoic acid or an acid isomeric with it.

A considerable time before Kekulé announced the formation of anthraquinone by the dry distillation of calcium benzoate (*Chem. Soc. J.* [2], xi, 171) the author had succeeded in obtaining several grams of perfectly pure anthraquinone this way.

This formation of anthraquinone shows that in the formation of ketones the process must be regarded as occurring in two stages. The first stage is (ca = $\frac{1}{2}$Ca; Kekulé)—

$$\begin{array}{l} C_6H_4.\ \ H\ \ \ COOca \\ C_6H_5.CO\ \ \ Oca \end{array} = \begin{array}{l} C_6H_4.COOca \\ \ \ \ \ | \\ C_6H_5.CO \end{array} + HOca;$$

and the second stage—

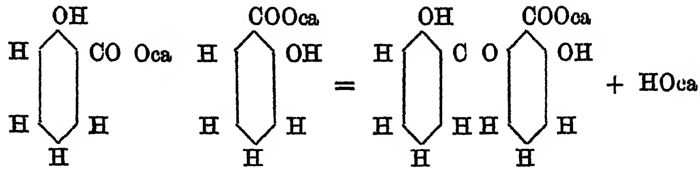
$$\begin{array}{l} C_6H_2.COOca \\ \ \ \ \ | \\ C_6H_5.CO \end{array} + HOca = \begin{array}{l} C_6H_5 \\ \ \ | \\ C_6H_5.CO \end{array} + CO_3Ca.$$

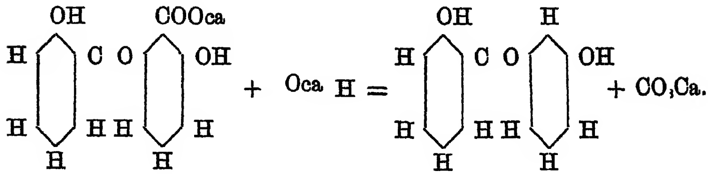
But the production of anthraquinone shows that the first stage may be repeated—

$$C_6H_4\begin{array}{l} H \\ \\ COOca \end{array} + \begin{array}{r} caOOC \\ \\ H \end{array}C_6H_4 = C_6H_4\left\langle\begin{array}{c} CO \\ CO \end{array}\right\rangle C_6H_4 + H_2OCa.$$

A similar view may be taken of the formation of aldehydes by the distillation together of organic calcium salts and calcium formate.

A substituted benzoic acid ought, according to this view, to yield an unsymmetrical ketone. Thus the ketone which can be obtained by the dry distillation of calcium salicylate will be formed as follows:—





The proof of the structure of this ketone would be that when fused with potassium hydrate it yielded, besides phenol, a mixture of potassium oxybenzoate and salicylate.

The splitting up of the ketones explains the process of decomposition of aldehydes by potassium hydrate. Thus in the production of potassium benzoate and benzyl alcohol by boiling oil of bitter almonds with alcoholic potash, the process must occur in two stages—

$$C_6H_5COH + HOH = C_6H_5COOH + H_2.$$
$$C_6H_5COH + H_2 \quad = C_6H_5CH_2OH.$$

So also the formation of benzilic acid from benzile by boiling it with alcoholic potash is easily explained—

$$\underbrace{C_6H_5\,CO.C_6H_4\,COH}_{\text{Benzile}} + KOH = C_6H_5.CO\,C_6H_4.COOK + H_2;$$

$$C_6H_5.CO.C_6H_4.COOK + H_2 = \underbrace{C_6H_5.CHOH\,C_6H_4\,COOK.}_{\text{Potassium benzilate}}$$

The stability of the aromatic carbon acids when fused with potassium hydrate on the one hand, and the possibility on the other, of forming these by the decomposition of ketones, presents us with a new method for the synthesis of the aromatic dicarbon acids, since it appears not improbable that benzoylbenzoic acid, or acids isomeric with or similar to it, may decompose when fused with potassium hydrate in the following manner:—

$$RCOR''COOK + KOH = RH + R''(COOK)_2.$$

E. D.

Decomposition of Ketones by Heat. By W. STAEDEL (Deut. Chem. Ges. Ber., vi, 189).

WHEN benzophenone is distilled over zinc-dust, a colourless oil is obtained, which becomes crystalline when cooled; addition of alcohol

gives a crystalline precipitate, which, when recrystallised from alcohol, furnishes fine colourless needles or thick plates, apparently belonging to the rhombic system; these melt at 199°—200°, and are almost insoluble in cold alcohol. The mother-liquors from which this precipitate was thrown down furnished an oil distilling almost entirely between 255° and 265°. Probably this is diphenyl-methane, $CH_2(C_6H_5)_2$, the crystalline mass being possibly—

$$\begin{array}{l} C(C_6H_5)_2 \\ \| \\ C(C_6H_5)_2 \end{array} = \text{diphenyl-ethylene, or } \begin{array}{l} CH(C_6H_5)_2 \\ | \\ CH(C_6H_5)_2 \end{array} = \text{diphenyl-ethane:}$$

$$\text{possibly } \left\{ \begin{array}{l} C_6H_4 \\ C_6H_4 \end{array} \right\rangle CH_2, \text{ or } \left\{ \begin{array}{l} C_6H_4 \\ C_6H_4 \end{array} \right\rangle C \left\langle \begin{array}{l} C_6H_4 \\ C_6H_4 \end{array} \right\} \text{might result.}$$

The products have not yet been analysed.

C. R. A. W.

A New Hydrocarbon from Diphenylene-ketone. By R. Fittig (Deut. Chem. Ges. Ber., vi, 187).

When diphenylene ketone $\left\{ \begin{array}{l} C_6H_4 \\ C_6H_4 \end{array} \right\rangle CO$ is distilled over zinc-dust, it is easily and completely reduced, forming a colourless hydrocarbon, easily soluble in alcohol, crystallising in shining scales or warty concretions, and melting at 113°—114°. This is doubtless diphenylene-methane, $\left. \begin{array}{l} C_6H_4 \\ | \\ C_6H_4 \end{array} \right\rangle CH_2$, and it will probably be formed by passing diphenyl-methane through a red-hot tube.

C. R. A. W.

Mellitic Acid. By A. Baeyer (Ann. Chem. Pharm., clxvi, 325—360).

The chief results of this elaborate paper have already been published in this Journal ([2], ix, 372). The present communication gives a full description of the preparation, modes of separation, and properties of the different acids, and contains besides the following new facts:—

Prehnitric anhydride has the composition $C_6H_2 \left\{ \begin{array}{l} CO \\ CO \end{array} \right\rangle O. \\ (CO_2H)_2$ The acid called formerly (*Ann. Chem. Pharm. Suppl.*, vii, 38) hydropyromellitic acid, is a mixture of two isomerides. One of these, for which the original name has been retained, is amorphous, whilst *isohydropyromellitic acid*, $C_{10}O_8H_{10} + 2H_2O$, crystallises in agglomerations of needles, which lose their water at 120°. Its aqueous solution is not precipitated by baryta-water in the cold, but on heating, a dense crystalline precipitate, soluble in acetic acid, is formed. Lead acetate produces a flocculent precipitate insoluble in acetic acid. The amorphous acid, as well as

the crystallised, yields tetrahydrophthalic acid when heated above 200°.

As the methyl-ethers of the different polycarbonic acids of benzene crystallise exceedingly well, they are well adapted for the detection and comparison of these acids. The following were prepared by acting with methyl iodide on the silver salts.

Methyl isohydropyromellitate crystallises from a hot alcoholic solution in short, thick needles, melting at 156°, and distilling without decomposition. *Methyl pyromellitate* is but sparingly soluble in boiling alcohol, and forms large plates melting at 138°. *Methyl trimellitate* forms a viscid mass. *Methyl isophthalate* crystallises from dilute alcohol in long, slender needles, melting at 63°—65°. When mellitic acid is heated with glycerin until the solid mass becomes brownish black and porous, no pyromellitic acid is formed, but a large quantity of trimesic acid.

Trimellitic acid yields, when heated, the anhydride, $C_6H_3\left\{\begin{matrix} CO \\ CO \end{matrix}\right\rangle O \atop CO_2H$, a crystalline mass, melting at 157°—158°, and dissolving readily in hot water. All experiments undertaken for the purpose of obtaining the acid $C_6H(CO_2H)_5$ failed.

C. S.

Chlorosalicylic Acid. By H. HUEBNER and O. BRENKEN (Deut. Chem. Ges. Ber., vi, 174).

THIS acid was obtained by passing the calculated quantity of chlorine into a mixture of 40 grams of salicylic acid and a large quantity of carbon disulphide. After three crystallisations from water, it was obtained in small white needles, melting at 172·5°.

$[C_6H_3Cl(OH)CO_2]_2Ba + 3H_2O$ is freely soluble in water and alcohol, and forms small needles with a splendid pearly lustre. It loses its water at 130°, becomes brown at 150°, and at 180° begins to glow and is carbonised. $[C_6H_3Cl(OH)CO_2]_2Pb$ is a heavy crystalline precipitate. $[C_6H_3Cl(OH)CO_2]_2Cu$ is not quite insoluble in water, and forms an amorphous greyish-green precipitate. $C_6H_3Cl(OH)CO_2Ag$ is a white precipitate, which blackens on exposure to light.

C. S.

Conversion of Benzoic Acid into Metachlorortho-oxybenzoic Acid. By H. HUEBNER and G. WEISS (Deut. Chem. Ges. Ber., vi, 175).

A VERY convenient way of obtaining pure monochlorobenzoic acid consists in heating 7 grams of benzoic acid with 4 grams of manganese dioxide and 40 grams of fuming hydrochloric acid in sealed tubes to 150°. When heated with fuming nitric acid, it yields only one mononitro-product, melting at 136°, and giving by reduction the amido-acid, which is only sparingly soluble in water, and forms long colourless needles, melting at 148°. On suspending it in water at 500°, and passing nitrous acid through the liquid, it is converted into metachlororthoxybenzoic acid,

which is identical with the acid obtained by the action of chlorine on salycylic acid (see preceding paper).

C. S.

Iodobenzene-parasulphonic Acid. By W. KOERNER and E. PATERNÒ (Gazzetta Chimica italiana, ii, 448—450, reprinted from the Giornale di Sc. Nat. ed Econom. for 1869).

IODOBENZENE, boiling at 190°, when heated to 100° with a mixture of equal parts of ordinary and fuming sulphuric acid, dissolves for the most part, forming iodobenzene-parasulphonic acid, only a small quantity of a solid substance being left. The latter, when purified by crystallisation, forms beautiful colourless lustrous prisms, apparently iodosulphobenzide, $C_6H_4ISO_2.C_6H_4I$. The sulphonic acid is purified by converting it into the lead salt $(C_6H_4ISO_3)_2Pb$, and recrystallising. This forms white silky needles, which are only slightly soluble in cold water. The free acid crystallises in colourless plates, which are very deliquescent. The potassium salt, $C_6H_4ISO_3K$, forms colourless prisms, very soluble in water. The barium salt $(C_6H_4ISO_3)_2Ba$, crystallises in plates. On fusing the potassium salt of this acid with potassium hydrate, resorcin is formed, but the best method of preparing the latter substance is to fuse with potassium hydrate, the potassium salt of phenolbisulphonic acid obtained by treating benzenesulphonic acid with fuming sulphuric acid.

C. E. G.

On Two Nitrophenolsulphonic Acids. By W. KOERNER (Gazzetta Chimica italiana, ii, 444—448; reprinted from the Giornale di Sc. Nat. ed Econom. for 1869).

THE author finds, from a careful examination of the nitrophenolsulphonic acid prepared by Kekulé (*Zeitschr. f. Chem.*, 1867, 641), by dissolving metanitrophenol in fuming sulphuric acid, and that obtained by Kolbe and Gauhe (*Ann. Chem. Pharm.*, cxlvii, 71), from potassium phenolsulphate, that the two are identical, and at the same time points out that the most advantageous method of preparing the acid is to treat potassium phenolparasulphate with dilute nitric acid.

The author then describes a new acid, the *orthonitrophenolsulphonic acid*, prepared by the action of fuming sulphuric acid on orthonitrophenol. The free acid crystallises in slender needles, or large colourless prisms, containing three molecules of water, which they lose at 100°. It forms two series of salts, neutral and acid, remarkable for the facility with which they crystallise. The *bipotassic* salt, $C_6H_3NO_2SO_2K.OK + H_2O$, crystallises in orange-coloured prismatic needles, which are very soluble in water; the *monopotassic* salt, $C_6H_3NO_2SO_3K.OH$, in colourless prisms, slightly soluble in water; the *bisodic* salt, $C_6H_3NO_2SO_3NaONa + 2H_2O$, and the *monosodic* salt, $C_6H_3NO_2SO_3NaOH + 2H_2O$, the two calcic, baric, and argentic salts are all described; the neutral salts are yellow, whilst all the acid salts are colourless.

C. E. G.

Action of Benzoic Acid on Phenylic Mustard-oil.

By S. M. LOSANITCH (Deut. Chem. Ges. Ber., vi, 176).

BY the action of acetic acid on this mustard-oil (phenyl-sulphocarbimide) Hofmann obtained phenyl-diacetamide. Benzoic acid gives an analogous reaction when the two compounds are heated in sealed tubes to 130°—150°:—

$$\left.\begin{matrix}C_6H_5\\CS\end{matrix}\right\}N + 2C_6H_5.CO.OH = \left.\begin{matrix}C_6H_5\\(C_6H_5.CO)_2\end{matrix}\right\}N + CO_2 + H_2S.$$

Phenyldibenzamide crystallises from alcohol in white crystals melting at 155°.

Salicylic acid does not act on phenylic mustard-oil at 200°.

C. S.

Chloracetyl Urea.

By D. TOMMASI (Bull. Soc. Chim. [2], xix, 243—245).

WHEN one molecule of urea is mixed with one molecule of monochloracetyl chloride, the mass soon becomes liquid and boils, hydrochloric acid is evolved in large quantities, and the sides of the vessel are covered with a white solid. The reaction, which is completed by heating in a water-bath, is as follows:—

$$\left.\begin{matrix}CO\\H_2\\H_2\end{matrix}\right\}N_2 + (C_2H_2ClO)Cl = HCl + \left.\begin{matrix}CO\\H_2\\(C_2H_2ClO)H\end{matrix}\right\}N_2.$$

The chloracetyl urea thus obtained crystallises in colourless needles insoluble in cold water and but little soluble in hot water, slightly soluble in cold, much more soluble in hot alcohol. It decomposes at 160°. When treated with fuming nitric acid in the cold, it gives off several gases, among which is carbon dioxide. It is slightly soluble in concentrated nitric, sulphuric, hydrochloric, and acetic acids. It is not precipitated by mercurous or silver nitrate. Nascent hydrogen does not, as it was expected it would do, convert it into acetyl-urea. When chloracetyl-urea is placed in the mouth, a burning sensation is produced in the throat, accompanied by a sharp pain and a difficulty in breathing. These symptoms, however, pass off in about an hour, and the new compound cannot be classed among the violent poisons, since a rabbit to which 0·1 gram had been administered showed no signs of suffering.

B. J. G.

Parabanic Acid.

By N. MENSCHUTKIN (Deut. Chem. Ges. Ber., vi, 196).

PARABANIC acid is capable of forming salts under somewhat unusual conditions. When a solution of this acid in absolute alcohol is treated with potassium ethylate, a potassium salt, $C_3HKN_2O_3$, is thrown down as a fine crystalline precipitate which is decomposed by water, with formation of potassium oxalate. Similarly a sodium and an ammonium salt can be obtained. The last decomposes on standing in the air-bath into ammonia and parabanic acid; when heated to 100° in an atmo-

sphere of ammonia, it becomes changed into the isomeric oxaluramide. The author concludes that parabanic acid is not a substituted urea, but is more analogous to cyanic acid. He proposes to study alloxan and barbituric acid.

C. R. A. W.

A Hydrate of Parabanic Acid.

By B. TOLLENS and R. WAGNER (Ann. Ch. Pharm., clxvi, 321—324).

THIS hydrate, having the composition $C_3H_2N_2O_3 + H_2O$, is always formed when uric acid is *gently* heated with nitric acid of sp. gr. 1·3, whilst when the action proceeds *violently*, the anhydrous acid is formed. The hydrate crystallises from water in large compact crystals resembling alloxan, whilst the anhydrous acid forms large flat needles. It loses its water only at 150°—160°, and the dried substance recrystallises from water in anhydrous needles. Whilst one part of the anhydrous acid dissolves in 21·2 parts of water at 8°, one part of the hydrate dissolves in 7·4 parts of water at the same temperature. These properties of the hydrate make it very probable that it does not contain water of crystallisation, but that it has the constitution $\begin{array}{l} C(OH)_2—NH \\ | \\ CO———NH \end{array}\!\!\!>CO.$

C. S.

On New Sources of Ethyl- and Methyl-Aniline. By J. SPILLER (Proc. Roy. Soc., xxi, 204—206).

IN the process of manufacturing the Hofmann violet by the action of ethylic or methylic iodide upon rosaniline or one of its salts, there is always produced a considerable quantity of a dark coloured resinous substance which has received the name of "Hofmann gum." When the water is expelled from this gum by fusion, and the residue is submitted to destructive distillation at a higher temperature,* it yields nearly pure methylaniline or ethylaniline, according as the gum has been derived from the methylic or ethylic iodide. The methylaniline is an oily body boiling at 200°, and forms permanently liquid compounds with acids. With arsenic acid it furnishes a reddish violet dye, which may be converted into the bluer shades by the Hofmann process. Ethylaniline boils at 205°—210°. Both these oils when heated with rosolic acid or rosaniline do not yield Girard's blue, but change slightly towards violet and then suddenly become decolorised, "a reaction almost without parallel in the history of the tinctorial aniline derivatives."

C. E. G.

On the Saccharine Matter contained in Mushrooms.

By A. MÜNTZ (Compt. rend., lxxvi, 649).

CERTAIN species of mushroom contain mannite; others a sugar identical with the trehalose which Berthelot obtained from an edible manna

* A mixture of pulverised iron borings, kaolin, and syrupy silicate of soda, forms an excellent lute for fixing on the head of the still, as it withstands a high temperature without softening.

imported from the East; others, again, contain both these sugars, and in very variable proportions; and some contain mannite, trehalose, and another sugar, the nature of which has not yet been fully determined. Botanical analogy affords no guide to the kind of sugar present, for in species closely allied, growing in the same soil and under the same conditions, some contain mannite only and others trehalose only.

J. B.

Nicotine in Tobacco Smoke. By HEUBEL (Chem. Centr., 1873, 101).

THE author conducted the smoke of cigars through water and alcohol, and obtained distinct evidence of the presence of nicotine in the solution, thus differing from previous experimenters on this subject.

W. S.

Curcumin.

By IVANOW GAJEVSKY (Deut. Chem. Ges. Ber., vi, 196).

BY oxidation with potassium dichromate and sulphuric acid, curcumin furnishes terephthalic acid. Rosocyanin contains no boron, and produces paraoxybenzoic acid by fusion with caustic potash.

C. R. A. W.

Researches on the Albuminoïds. By OTTO NASSE (Pflüger's Archiv. f. Physiologie, vi, 589—616, and vii, 139—155).

NASSE considers that the chemical constitution of the albuminoïds has been too much neglected in the study of their physical characters. He has, therefore, undertaken a research on the constitution of these substances. His method consists in acting on them with caustic baryta, which has an advantage over caustic alkalis, inasmuch as its action does not vary with the degree of concentration. The finely powdered albuminoïds were heated with barium hydrate and water for about fifty hours, and the ammonia evolved received in dilute sulphuric acid. Only a part of the nitrogen was evolved, and the quantity varied for each albuminoid within certain limits. The whole quantity of nitrogen was also determined by combustion with soda-lime, and titration of the ammonium chloride with silver solution. The whole quantity of nitrogen divided by the loosely combined nitrogen driven off by caustic baryta gives characteristic quotients for the various albuminoïds. Tables are given of the various quotients so obtained from the different albuminoïds, the exact method of preparing which is also given. The smallest quotient is given by casein (0·112), and the largest by gluten (0·30), *i.e.*, gluten contains a much larger quantity of loosely combined nitrogen than casein. In his first paper, Nasse states that the quotient for syntonin varies according to the method of its preparation. Syntonin (A) prepared by acting on albumin with dilute hydrochloric acid, differs from that obtained by the action of concentrated acid, and the syntonins (B′) prepared from coagulated albumin differ from the syntonins (B) obtained from non-

coagulated albumin. He states that the A syntonins are richer in loosely combined nitrogen than the mother-substances, while the B and B′ syntonins are poorer, and that these two latter differ from each other. In his second paper, in which he follows a new method, Nasse states that there is really no difference between the two latter, and he classes them together. The new method consists in heating albuminoïds with hydrochloric acid, and driving off the acid as much as possible. The albuminoïds are completely decomposed, and nitrogenous substances are produced, such as ammonium chloride, leucine, tyrosine, glycocine, and, as Hlasiwetz has shown, glutamic acid; in short, substances which give off their ammonia readily on the addition of an alkali, and substances which do so with difficulty. This mixture treated with barium hydrate allows of comparative determinations being made as regards the amount of nitrogen liberated.

New tables are given of the quotients obtained by this method. The only remarkable difference between these and the former is that the quotients are much smaller. The difference between the richer and poorer in loosely combined nitrogen is now seen to be greater. The position of some of the albuminoïds is also altered in the second table.

By comparison of the various results, it would appear that one part of the nitrogen is combined like the nitrogen in urea, *i.e.*, united in the form of an amide with carbonyl. The greater part of the remaining nitrogen is combined like the nitrogen in the amido-acids, *i.e.*, in the form of an amide with a hydrocarbon. A third part of the nitrogen is probably combined like the nitrogen in creatine, uric acid, &c.

Some speculations are given as to the changes which the albuminoïds undergo in the organism with regard to their loosely combined nitrogen, but for these we would refer the reader to the original paper.

D. F.

Iodine Substitution-products. By P. WESELSKY (Deut. Chem. Ges. Ber., vi, 176).

Physiological Chemistry.

On Pepsin and the Digestion of Fibrin without Pepsin. By G. WOLFFHÜGEL (Pflüger's Archiv., vii, 188—200).

THE author has obtained results which are somewhat at variance with those arrived at by v. Wittich in regard to the diffusibility of pepsin. After giving details of his experiments, he thus sums up his principal conclusions :—

1. Pepsin is not diffusible.
2. The pyloric glands do not produce pepsin. (In this he agrees with Friedinger, Fick, and v. Wittich.)
3. Hydrochloric or nitric acid diluted to 0·4 per cent. is able to convert boiled fibrin into peptones at a temperature of 60°. The change however takes place very slowly.

4. The power possessed by these acids of forming peptones begins to show itself at 40°, but more slowly in the case of nitric than of hydrochloric acid.

5. For this reason nitric acid is to be preferred to hydrochloric acid for the detection of pepsin.

D. F.

Experimental Researches on the Influence of Change in Barometric Pressure on the Organism. (Ninth Note.) By P. BERT (Compt. rend., lxxvi, 578—582).

M. BERT directs his attention in the present communication to the causes and prevention of the spinal softening and paraplegia which result from the sudden diminution of the pressure in the case of animals and divers who have been subjected to a pressure of many atmospheres. As he has shown, the effects are due to the liberation of nitrogen from the blood, which in small quantity interrupts the circulation in the lumbar region of the cord, and in larger amount embarrasses the heart and lungs and leads to a fatal result. Considerable differences exist between different animals and the same animal at different periods in regard to the effect of suddenly diminishing the pressure. In reference to these differences he finds that in dogs the blood is saturated with nitrogen when the animal is breathing at the normal barometric pressure. Bubbles of gas begin to appear at three atmospheres, but accidents do not usually occur till the pressure has reached seven atmospheres. Between these two points, however, the animal is continually in danger, and a combination of circumstances may cause such an accumulation of the gas as to lead to the dangers specified.

In one experiment the sudden bursting of the receiver when a dog was under a pressure of nine and a-half atmospheres caused instant death of the animal. In this case not only were the vessels filled with bubbles of gas, but bubbles were also found in the peritoneal cavity, together with general emphysema of the subcutaneous and intermuscular cellular tissue. Hence the gas becomes dissolved in and ultimately liberated from the other fluids of the body as well as the blood itself. Some of the affections to which divers are liable (*puces*, *mouton*) are due to cellular emphysema so caused. In order to avoid these dangers a gradual diminution of the pressure would seem indicated, or a restoration of the pressure when evil results occur. But the difficulty of rapidly raising the pressure again may endanger the life of the animal in the meantime. A sudden re-descent into the water would seem to be beneficial to divers. In the cases where this procedure cannot be carried out at once, M. Bert recommends the inhalation of oxygen in order, to allow of rapid diffusion and the disappearance of the bubbles of nitrogen, and in this way to restore the circulation and respiration to their normal condition.

D. F.

The Toxic Effects of the Iodides of Tetramethylammonium and Tetramylammonium. By RABUTEAU (Compt. rend., lxxvi, 887—890).

THE author has found that whilst the salts of the primary, secondary, and tertiary amines are comparable in their physiological effects to ammoniacal salts, and are muscular poisons, the salts in which all the four hydrogen atoms of ammonium are replaced by alcohol radicals, such as those of tetramethylammonium, paralyse the motor-nerves, and are similar to curare in their effects.

T. S.

Alcohol and Acetic Acid normally present in Milk as Products of the Functions of Microzymes. By A. BÉCAMP (Compt. rend., lxxvi, 836—839).

REFERENCE is made to a previous memoir by the author, showing the necessary presence of microzymes in milk, as agents bringing about the spontaneous coagulation of that secretion. The present note demonstrates the presence of alcohol and acetic acid in fresh milk, and of an increased quantity of those substances after coagulation of the liquid.

A sufficient quantity of alcohol was obtained from fresh milk to permit the verification of the nature of the product by its inflammability, the products of its oxidation by chromic acid, the formation of crystals of sodium acetate from it, and the analysis of these crystals.

Acetic acid was also obtained from the residue after the alcohol had been distilled off; and the acid was converted into sodium acetate and crystallised. None of the higher homologues of acetic acid were obtained.

It is concluded from further experiments that alcohol exists in the milk of all the herbivora. Its presence has not yet been looked for in the milk of carnivorous animals. As much as 0·224 gram of alcohol was found in a litre of the fresh milk from a cow, and 0·62 gram in a similar milk which had stood for five days.

The author surmises that the alcohol and acetic acid formed in milk are generated in the mammary gland by the action of microzymes.

T. S.

Experiments relating to Putrefaction, Disinfection, and the Preservation of Organic Substances. By LANJORROIC (Compt. rend., lxxvi, 630).

THE author finds that 1 per cent. of fuchsine added to a solution of gelatin entirely prevents its putrefaction, a quantity prepared in this manner having been kept eleven months without change. A piece of meat wrapped in paper imbued with this prepared gelatin and suspended in a current of air, dried up but did not putrefy. After maceration for 24 hours this dried muscular fibre was found not to be disintegrated, neither had it any disagreeable odour. The addition of a very minute quantity of aniline-violet, urine, or an infusion of coffee, was also found to prevent its putrefaction entirely.

C. E. G.

Chemistry of Vegetable Physiology and Agriculture.

Chemical Researches on the Cyclamen. By S. De Luca (Gazzetta chimica italiana, ii, 556—563).

The tubers of *Cyclamen europæum* contain a fermentable saccharine substance, starch and gum, together with acrid and poisonous principles, the most abundant of which is a non-azotised glucoside, called cyclamin, prepared and described about 15 years ago, by de Luca (*Il nuovo Cimento*, v, 225; viii, 182), and by Martius (*N. Repert. Pharm.*, viii, 338). See also Watts's Dictionary (ii, 294). De Luca originally prepared this substance by repeatedly exhausting the tubers with alcohol; but this treatment is very tedious, and, in the present paper, a more expeditious method is given, founded on the property which cyclamin exhibits of coagulating like albumin when its aqueous solution is heated. The expressed juice of the tubers heated nearly to the boiling point, throws up to the surface a white flocculent substance, which may either be skimmed off, or separated by filtering the hot liquid. This substance dissolves in hot alcohol, and the solution filtered while still hot, deposits the cyclamin on cooling in the amorphous aggregations were described in the author's former paper.

The present memoir adds but little to the description of the properties of cyclamin previously given, further than to indicate its points of resemblance to other proximate vegetable principles. It resembles albumin in its property of coagulating by heat; certain organic calcium-salts in the redissolution of the coagulum in the mother-liquor after cooling and remaining at rest for a few days, and its re-coagulation on boiling; mannite in its mode of separation from alcoholic solutions; saponin in the frothing of its aqueous solution; curarine in its action on the animal economy; salicin and glucosides in general in its re-solution by dilute acids into glucose and cyclamiretin.

Cyclamin contains, according to De Luca, 54·5 p.c. carbon and 9·1 hydrogen, agreeing exactly with the formula, C_2H_4O; according to an analysis by Klinger, it contains 55·2 carbon, and 7·8 hydrogen, agreeing with the formula, $C_{20}H_{34}O_{10}$. According to the latter formula, its decomposition into glucose and cyclamiretin may be represented by the equation:

$$C_{20}H_{34}O_{10} + 2H_2O = C_6H_{12}O_6 + C_{14}H_{26}O_6.$$

The juice of the tubers of cyclamen left to itself for some days, in contact with the air, soon ferments, with evolution of carbon dioxide and formation of alcohol; the cyclamin in the solution is at the same time coagulated by the heat resulting from the fermentation. The filtered liquid, evaporated to dryness over the water-bath, leaves a brownish residue, the solution of which in cold alcohol yields by spontaneous evaporation crystals of mannite. This substance may also be extracted by treating the above-mentioned residue with hot alcohol, and leaving the solution to cool. It appears to be a product of the fermentation above-mentioned, for the unfermented juice does not yield a trace of it. Further experiments are required to decide

whether the mannite is formed by transformation of the cyclamin, or of some of the other substances contained in the juice.

Other saccharine substances more or less resembling mannite have been obtained from the juice of cyclamen. The coagulum obtained by boiling a large quantity of the juice was collected on filters, and these, after the liquid had drained away, were placed under a bell-jar and surrounded by lumps of quicklime renewed as they slaked. After some weeks, the whole of the coagulum was found to be converted into a crystalline substance exhibiting some of the properties of mannite. Another portion of the expressed juice poured into large glass vessels, began, after ten days, to deposit on the side more directly exposed to the light, a white amorphous substance which gradually increased in quantity. On boiling the remaining liquid, only a small quantity of coagulum was obtained, and on separating the liquid therefrom, evaporating to dryness, and treating the blackish residue with hot alcohol, a solution was obtained which gradually deposited a crystalline substance likewise resembling mannite in some of its characters. The remaining portion of the expressed juice evaporated over the water-bath, left a residue from which cold alcohol extracted unaltered cyclamin.

These experiments seem to show that cyclamin is capable of gradually changing, under the influence of moisture, into a sweet crystallisable substance similar to, if not identical with, mannite. Further investigations on this transformation are promised.

The juice of cyclamen may be introduced into the stomach of rabbits in doses of 10 to 20 grams without destroying life, and the tubers are eaten without injury by pigs, but the juice mixed with water (1 cub. cent. to 2 or 3 litres) acts poisonously on fishes. The toxic action of cyclamin is similar to that of curarine, but less energetic, and like the latter may be nearly neutralised by bromine.

H. W.

New Genus of Plants capable of Precipitating Calcium Carbonate. By F. WIBEL and E. ZACHARIAS (Deut. Chem. Ges. Ber., vi, 182).

ALL the plants hitherto known to precipitate calcium carbonate from natural waters belong to the cryptogamia. The authors now find that the large species of Potamogeton do the same. The leaves become encrusted with crystalline hydrated calcium carbonate. This they have observed to occur in the waters of the Bille, a rather considerable stream emptying itself into the Elbe near Hamburg.

A hundred litres of this water contain—

	grams.
$CaCO_3$	6·18
$CaSO_4$	9·71
NaCl	6·60
Insoluble	0·60
Organic matter and combined water (loss on ignition)	15·00
	35·09*
Solid residue found	35·00

* There is an error in these numbers.—ED.

The yellowish water contains numerous flocculi consisting of mud and calcareous algæ, and deposits these upon all objects. But the incrustation above referred to is quite independent of this. The leaves on the surface of the water, as of *Potamogeton rufescens*, do not become thus coated, even on their under-surfaces, while the submerged leaves become completely encrusted. The formation of the crust is attributed by the authors to the absorption of carbon dioxide from the water of the leaves. The cause of the non-precipitation on the leaves in contact with the atmosphere is obvious upon this view of the matter.

E. D.

On the Assimilability of Phosphates. By H. JOULIE (Compt. rend., lxxvi, 631).

THE assimilability of phosphates is, according to the author's experiments, proportional to the facility with which they are decomposed by ammonium oxalate, and in certain instances to their solubility in acetic acid. He finds by these methods that the phosphates of the south of France, of the same richness, are more readily assimilated than those of the Ardennes, and suggests that agriculturists should direct their attention to this matter, since the efficacy of the phosphates depends more on this than on the percentage of phosphoric acid actually present.

C. E. G.

Analyses of Agricultural Materials. By A. VOELCKER (Jour. Roy. Agri. Soc. [2], ix, 258—268).

THE guano from the Guanape Islands averaged last year about 10 per cent. of nitrogen and 30 per cent. of phosphates; a few cargoes from Macabi Island had a similar composition. A sample of guano from Patagonia contained 4·42 per cent. of nitrogen and 22 per cent. of phosphates; it was very damp. Mejillones guano is a valuable phosphatic guano containing 74 per cent. of phosphates and 0·9 per cent. of nitrogen. Guano from Curaçao gave 73 per cent. of phosphates. Both these guanos are admirably adapted for the manufacture of superphosphate. Peruvian guano is treated at Hamburg on a large scale with small quantities of sulphuric acid to fix the ammonium carbonate; samples of guano thus treated gave 21 per cent. of soluble phosphates and nearly 9 per cent. of nitrogen.

Dried meat-fibre, the residue from the manufacture of Liebig's extract, has been imported as a manure; a sample from South America contained 12 per cent. of nitrogen, another from Australia 11 per cent., a third sample from New Orleans, called "Azotene," gave 11·3 per cent.; the samples gave very little ash.

A sample of night soil, prepared by Goux's patent gave 0·94 per cent. of nitrogen and 1·31 per cent. of phosphates.

R. W.

Pure and Mixed Linseed Cake. By A. Voelcker (Jour. Roy. Agri. Soc. [2], ix, 1—51).

Best linseed contains about 4 per cent. of weed-seeds, the amount rising to 40 per cent., or more, in inferior and adulterated samples. Of these seeds 23 species are described, of which *Linum catharticum*, *Lolium temulentum*, *Sinapis arvensis*, and *Githago segetum* are more or less injurious, and others, as *Raphanus Raphanistrum* and *Camelina sativa*, possess a disagreeable flavour. Nitrogen was determined in eight species. *Sinapis alba* contained 3·99; *Camelina sativa*, 3·46; *Sinapis glauca*, 2·96; *Githago segetum*, 2·56; *Chenopodium*, 2·56; *Centaurea Cyanus*, 2·31; *Lolium temulentum*, 1·89; and *Spergula arvensis*, ·90 per cent. of nitrogen.

Baltic linseed generally yields the best feeding cake; the cake is darker, more nitrogenous, and gelatinizes more with water than that made from Bombay seed. American and Marseilles cake are generally pure, but rather hard-pressed; Hungarian and Neapolitan cake frequently contain oats and other grains. Thin cakes generally contain less oil than thick ones.

Linseed cake is often largely contaminated by the weed-seeds in the linseed, and by admixture with other seeds or cakes; the composition of most of the ingredients of mixed cakes is shown in the accompanying tables (p. 768), the ingredients chiefly used as admixtures are marked*.

Indian rape usually contains so much mustard as to be injurious to animals; in composition it is similar to German rape. Beech-nut cake contains a volatile narcotic principle, said to be injurious. Cocoa-bean cake is made from the shells, the kernels being used for chocolate. Palm-nut cake is made from the fleshy part of the fruit of the oil-palm; palm-kernel cake is prepared from the kernels of the same fruit. Niger, or Gingelly cake, is made from the seed of the *Guizotea oleifera*. Olive cake varies much in composition (compare page 403 of this volume). Castor-oil cake contains as much as 8·69 per cent. of nitrogen, it is injurious to cattle, but excellent as manure. Curcas beans (*Jatropha Curcas*), are highly poisonous, but are, notwithstanding, occasionally found in feeding cakes. Siftings cake is prepared from the screenings of dirty linseed. Locust-beans contain half their weight of sugar; cakes containing them are liable to attract moisture and become mouldy. The husks of Brassia nuts are acrid, and the cake unfit for food. Dari grain is the seed of *Andropogon Sorghum*. Cocoa-nut fibre and other rubbish, are also found in feeding-cakes. Foreign ingredients are best detected by the microscope; numerous drawings of magnified sections are given in the paper. As linseed contains no starch, iodine serves to detect bran and starchy seeds.

Feeding-cakes which produce poisonous effects, but do not contain any of the injurious substances above-mentioned, generally owe their action to the mouldy condition of some of their ingredients.

R. W.

Percentage Composition of Linseed, and of some Ingredients of Mixed Cakes.

	Linseed. Highest percentages	Linseed. Lowest percentages	Locust beans *	Brassia nuts.	Dari grain.	Acorns (decorticated).	Rice meal *	Bran *	Rice husks.	Oat husks.	Flax chaff.	Palm-kernel shells
Moisture	10·61	5·47	14·64	6·51	18·14	40·88	8·67	12·86	9·80	11·98	14·60	10·12
Oil	38·21	30·78	1·08	10·40	3·30	2·64	7·59	5·56	1·10	·36	2·82	1·51
Albuminoids	26·62	19·31	7·03	9·31	7·75	4·39	7·75	13·80	4·18	1·25	4·75	2·93
Soluble carbo hydrates	26·22	17·80	65·03	32·41	68·15	46·74	39·98	50·17	41·91	53·63	27·28	16·37
Woody fibre	11·40	5·91	6·31	8·24	4·72	3·94	21·98	11·50	26·80	28·48	43·12	67·90
Ash	4·57	2·76	2·88	3·10	2·61	1·41	14·03	6·11	13·18	4·30	7·43	1·17
Nitrogen	4·26	3·09	1·13	1·49	1·21	·70	1·24	2·24	·67	·20	·76	·47

Percentage Composition of Cakes used for Feeding Purposes

	Linseed. Highest percentages	Linseed. Lowest percentages	Rape (German) *	Cotton seed. Undecorticated	Cotton seed. Decorticated	Earth-nut.* Undecorticated	Earth-nut.* Decorticated	Sesamé *	Niger-seed *
Moisture	14·93	9·44	10·82	11·46	9·28	8·10	9·26	8·06	12·56
Oil	15·84	9·88	8·72	6·07	16·05	8·76	5·58	11·34	5·38
Albuminoids	35·31	23·25	33·81	22·94	41·25	30·50	43·43	36·87	32·81
Soluble carbo hydrates	36·86	20·06	28·05	32·52	16·45	27·78	31·39	25·05	20·31
Woody fibre	15·38	8·38	11·49	20·99	8·92	19·12	5·18	8·11	21·08
Ash	8·73	5·40	7·10	6·02	8·05	5·71	5·16	10·51	7·86
Nitrogen	5·65	3·72	5·41	3·67	6·58	4·88	6·95	5·90	5·25

	Hemp.	Poppy.	Palm-nut	Palm-kernel (foreign)	Beech-nut	Cocoa-nut	Cacao bean	Indigo-seed	Linseed siftings.	Olive.
Moisture	11·59	11·68	8·67	11·91	11·44	8·97	14·95	11·91	10·57	18·41
Oil	7·23	5·75	9·82	7·48	5·22	11·44	8·02	4·01	6·45	3·10
Albuminoids	33·50	31·46	35·56	18·25	18·81	20·75	19·87	18·15	18·44	6·01
Soluble carbo hydrates	15·56	38·18 (soluble carbo hydrates and woody fibre)	18·50	41·16	36·17	39·41	32·46	47·96	35·94	30·66
Woody fibre	23·74		17·05	17·05	23·52	14·27	18·26	11·88	14·18	38·24
Ash	8·38	12·98	10·40	3·30	4·84	5·16	6·44	6·09	14·47	8·58
Nitrogen	5·36	5·11	5·69	2·92	3·01	3·32	3·18	2·90	2·95	·96

PROCEEDINGS

AT THE

MEETINGS OF THE CHEMICAL SOCIETY,

SESSION 1872–73.

November 7th, 1872.

Dr. Williamson, Vice-President, in the Chair.

The following gentleman was duly elected a Fellow of the Society:—
Archibald Liversidge.

The following papers were read:—

"On the Action of Charcoal on Organic Nitrogen:" by E. C. Stanford.

"On Iona Pebbles:" by E. C. Stanford.

"Mineralogical Notices:" by N. Story-Maskelyne and Dr. Flight.

"On the Specific Heat of Occluded Hydrogen:" by W. Chandler Roberts and Dr. C. R. A. Wright.

"On a means of Preventing Explosions in Coal Mines:" by J. A. Newlands.

"On some Possible Reactions that yielded Negative Results:" by Dr. C. R. A. Wright.

November 21st, 1872.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—
Arthur Willis, Robert S. G. Paton.

The following papers were read:—

"On the Standardising of Acids:" by W. N. Hartley.

"On Anthraflavic Acid:" by W. H. Perkin.

December 5th, 1872.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Kigonari H. Yoshida; Francis H. Hobler; Sydney Lupton; E. W. Prévost; Joseph Lainson Wills; Robert William Jones; A. Cameron Bruce; John Hollings Mitchell; Philip Braham; A. Percy Smith; S. D. Titmas; Thomas Williams.

The following papers were read:—

"On the Hypophosphites," and "On the reducing power of Phosphorus and Hypophosphorous Acids and their Salts:" by C. Rammelsberg.

"New Analyses of certain Mineral Arseniates and Phosphates:" by A. H. Church.

"On the condition of Hydrogen occluded by Palladium, as indicated by the Specific Heat of the charged Metal:" by W. Chandler Roberts and C. R. A. Wright.

December 19th, 1872.

Dr. Williamson, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Alfred Payne; George Combe Stewart; Robert Routledge; George B. Beelby.

The following papers were read:—

"On the Analysis of Water of the River Mahanuddy:" by E. Nicholson.

"Researches on the Polymerides of Morphine and their Derivatives:" by E. Ludwig Mayer and Dr. C. R. A. Wright.

"Communications from the Laboratory of the London Institution:" by Dr. H. E. Armstrong.

"On the Formation of Naphthaquinone by the direct Oxidation of Naphthalene:" by C. E. Groves.

January 16th, 1873.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

George Washington Arnott; James Scott McGregor; Cornelius A. Mahony.

The following papers were read:—

"Notes on various Chemical Reactions:" by Mr. Davies.

"On Ethyl-amyl:" by Harry Grimshaw.

"The Heptanes from Petroleum:" by Dr. Schorlemmer.

"The Vanadates of Thallium:" by T. Carnelley.

"On the Formation of Sodium Sulphide by the Action of Hydrogen Sulphide upon Sodium Chloride at High Temperatures:" by T. Kingzett.

February 6th, 1873.

Dr. Williamson. Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Charles Lees; John A. Bower; Miles H. Smith; George F. Schacht; Alfred J. Cownley; Walter E. Koch.

The following papers were read:—

"On the Action of Sodium on Aniline:" by H. E. Armstrong.

"On Anthrapurpurin:" by W. H. Perkin.

"Isomerism in the Terpene family of Hydrocarbons:" by C. R. A. Wright.

February 20th, 1873.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Waldron Shapleigh; Edward Dillon; John Perry; G. Brownen; T. W. Sheppard; J. C. Sellars; and H. Y. Loram.

The following papers were read:—

"On the Solidification of Nitrous Oxide:" by T. Wills.

"On Aurin," by R. S. Dale and C. Schorlemmer.

"Researches on the Action of the Copper-Zinc Couple on Organic Bodies. I. On Iodide of Ethyl:" by Dr. Gladstone and A. Tribe.

"On the Detection of Ammonia in the Atmosphere:" by A. H. Smee, jun.

March 6th, 1873.

Dr. Gladstone, Vice-President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

George Ainsworth; Alexander Bottle; R. J. Deeley; and J. W. Montgomery.

The following papers were read:—

"Action of Hydrochloric Acid on Codeine:" by C. R. A. Wright.

"On a method of Estimating Nitric Acid:" by T. E. Thorpe.

"Note on a Reaction of the Acetates upon Lead Salts, with remarks on the Solubility of Lead Chloride:" by F. Field.

"Observations on the Nature of the Black Deposit in the Copper-Zinc Couple:" by Dr. Gladstone and A. Tribe.

"An Air-bath of constant Temperature between 100° and 200° C.:" by H. Sprengel.

"On New Processes for Mercury Estimation, and some Observations on Mercury Salts:" by J. B. Hannay.

March 20th, 1873.

Dr. Frankland, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Andrew F. Crosse; Thomas Fulcher Best; W. Ramsay; James William Bantock; and Frederick Douglas Brown.

Dr. C. W. Siemens delivered a lecture "On Iron and Steel."

Anniversary Meeting, March 31st, 1873.

Professor Frankland, President, in the Chair.

The following Address was read by the President:—

GENTLEMEN,

On behalf of your Council, I have now the honour to lay before you a statement of the position of the Chemical Society at the end of our thirty-second year.

Your Council have again, as at the last Anniversary, the gratification to report the continued and increasing prosperity of the Society. I have once more to record that the addition to our numbers since the last Annual Meeting has been much larger than in any former year since that in which the Society was founded. Although we have lost during the year no fewer than 18 Fellows from various causes, our roll of home members still exhibits the large increase of 58 names, as shown by the following statement:—

Number of Fellows (Anniversary), March 30th, 1872......		624
Since elected, and paid admission fees		76
		700
Withdrawn: Robert Mallett, Esq., F.R.S., and A. N. Palmer, Esq..................	2	
Removed on account of arrears.................	6	
Deceased	10	
		18
Number of Fellows March 31st, 1873		682
Number of Foreign Members (Anniversary), March 30th, 1872		32
Present number of Foreign Members....................		32

Since our last Anniversary we have lost by death the following Fellows:—Thomas Bloxam, John Cargill Brough, Ernest Theophron Chapman, Professor John Hunter, Dr. Leeson, F.R.S., Frederick Muspratt, Robert Rumney, B. C. Staples, T. Thomas, and J. C. Wilson.

Thomas Bloxam was born in London in 1836, and received his early education at the City of London School, where he acted as lecture-assistant to Mr. Thomas Hall, the lecturer on experimental science. After leaving school he devoted himself to the study of chemistry, under the guidance of his elder brother, and in 1854 he was received, through the kindness of the late Professor W. A. Miller, into the laboratory of King's College, where he relieved his brother of some of his duties as Demonstrator of Chemistry.

In 1855 the late Dr. George Wilson, then director of the Industrial Museum of Scotland, nominated Bloxam for the appointment of assistant chemist, which he held until the death of Dr. Wilson in 1859, when the appointment was abolished. Those who knew Dr. Wilson will easily believe that he treated his young assistant with paternal kindness.

Returning to London, Bloxam engaged in private practice as an analytical chemist, and became lecturer on chemistry at the School of Medicine known as Lane's School, until 1862, when he had the good fortune to be recommended by Dr. Atkinson as his successor in the appointment of Lecturer on Experimental and Natural Science in Cheltenham College. Here Bloxam devoted himself, with only too great zeal, to the instruction of his pupils, with whom his genial and manly disposition and his love for athletic exercises made him a general favourite.

In July, 1872, he came to town in order to visit his brothers in

in London and Woolwich, and died very suddenly from an affection of the heart, which seized him in the street. He married, in 1863, Janet, daughter of Robert Scott, Esq., of Edinburgh, and left two children.

Bloxam was the author of the following papers, read before the Royal Society of Edinburgh :—

"On the composition of the Glassy Surface of some Vitrified Forts;"

"On the composition of old Scotch Glass;"

"Analysis of Craigleith Sandstone;"

and of short communications addressed to the British Association and the Chemical News.

During the last few months of his life he was engaged in a minute examination of the Cambray saline spring at Cheltenham, having evaporated 55 gallons of water for the purpose. His note-book shows that he had detected iodine, boracic acid, and lithium in appreciable quantity, but only a trace of bromine. Cæsium and rubidium had been sought for in vain.

Thomas Bloxam was elected to the Fellowship of the Chemical Society in 1859, and to that of the Geological Society in 1869.

John Cargill Brough was born in Pontypool, Monmouthshire, February 11, 1834. His father was then a brewer and wine merchant in that town, and also part owner of a coal mine in the neighbourhood.

In 1840 Mr. Barnabas Brough was one of the principal witnesses for the Crown in the trial of John Frost, the chief instigator of the Chartist movement in that district. In consequence, he became exceedingly unpopular among the pitmen and others who had been concerned in the outbreak, so much so, that they by degrees deserted the inns which he supplied, and in a short time his once prosperous business declined, and he was ultimately obliged to leave the town.

In 1845 Mr. Barnabas Brough received an appointment in the office of the *Illustrated London News*, and John, then a mere boy, became his father's assistant, and remained for some years in the office. During that time all his hours were spent in study. The love of science developed itself at a very early age, and many a time was it a matter of grave consideration how many pence could be saved out of his never too plentiful dinner money towards buying some much desired book, materials for experiments, or admission to a lecture.

In 1852 he became a clerk in the Audit Office of the South Western Railway Company, and while in that position became Secretary and Librarian of the Literary and Scientific Institution established by the Railway Company for its officials. Here he gave elementary lectures

on chemical and physical subjects. In 1854 he had the misfortune to lose his father, and at once had to lend his slender aid towards the maintenance of a younger brother and sisters.

His inclination to literary work caused him in 1857 to resign his situation that he might follow literature as a profession, writing articles on literary and scientific subjects for various magazines and periodicals. In 1859 he published "Fairy Tales of Science," and in 1860 he became and continued for ten years editor of the *Chemist and Druggist*, and in that capacity raised the character of the journal immensely. In 1864 he edited an edition of "Cooley's Cyclopædia of Practical Receipts," and about the same time was elected a Fellow of the Chemical Society, having previously trained himself in practical chemistry in the laboratory of a friend. In April, 1867, Mr. Brough started the *Laboratory*, a journal of physical and chemical science, which, on account of its excellence, immediately received the approbation and adhesion of most of the scientific men of the day. The particular section of the public to which it appealed was, however, not sufficiently numerous to make the proceeds cover the large outlay necessary for its publication, and it proved a commercial failure. During the Exeter meeting of the British Association in 1869, in conjunction with two friends, he published "Exeter Change," a humorous brochure, and when *Nature* was first published he was its sub-editor, but after a few months of careful work was compelled by an attack of illness to relinquish the post; but he continued to write reviews and articles on scientific subjects for several of the leading journals.

In 1870 he was appointed Librarian and Superintendent of the London Institution, a position for which he was eminently fitted, both on account of his literary and scientific acquirements, and of his natural courtesy and geniality of disposition. He became exceedingly popular with the frequenters of the Institution, doing much valuable work there, particularly with regard to lectures and examinations. During the winter of 1871–2 he gave a course of holiday lectures at the Institution on the Philosophy of Magic.

Mr. Brough had suffered for some years more or less from the effects of heart disease, the result of a severe attack of rheumatic fever which was nearly fatal to him when a boy, and finally sank on the 7th of September, 1872.

The handsome sum of £2,000 subscribed for the benefit of Mr. Brough's children is an honourable testimony to the universal esteem and regard in which he was held.

Ernest Theophron Chapman was born at Clapton, March 9, 1846. Frequent ill health interfered with his regular education, but studious and observant habits, even as a child, compensated to a great

extent for this drawback. His tastes were early directed to chemistry. At the age of fourteen, when suffering from inflammation of the eyes, he selected Miller's "Elements of Chemistry" as one of the books for his mother to read aloud to him. When fifteen, he was sent to a school at Heidelberg, where he attended the lectures of Professors Bunsen and Delffs, and he subsequently studied at the Royal College of Chemistry, first under Hofmann and afterwards under Frankland. He was also a student at the University of Marburg, under Kolbe. He contributed the results of numerous researches to the Chemical and Royal Societies, amongst the more important of which the following may be enumerated:—

1. The relation between the products of Gradual Oxidation, and the molecular constitution of the bodies oxidised.
2. Quantitative Analysis by Limited Oxidation.
3. Limited Oxidation: determination of the Oxygen consumed.
4. Oxidation of the Acids of the Lactic series.
5. On Limited Oxidation by Alkaline Permanganate.
6. On the Oxidation of Ethyl-crotonic Acid.
7. Production of Acetic and Propionic Acids from Amylic Alcohol.
8. On some decompositions of Nitrate of Amyl.
9. Nitrous and Nitric Ethers.
10. Action of Zinc-ethyl on Nitrous and Nitric Ethers.
11. On the estimation of Nitric Acid in Potable Waters.
12. On Caprylic and Œnanthylic Alcohols.
13. On the artificial production of Pyridine.
14. On a new Synthesis of Formic Acid.

He was also the joint author, with Mr. Wanklyn, of a "Practical Treatise on the Examination of Potable Waters." In August, 1869, he accepted an engagement in Germany as manager of a chemical factory in the Hartz Mountains, a position he retained till the unfortunate explosion which ended his life on June 25, 1872. Of the cause of this, nothing is known, beyond the fact that he had been engaged in preparing large quantities of methylic nitrate, to be used in blasting and other similar operations as a substitute for dynamite. Three workmen who were with him at the time of the accident also perished, and there was no survivor to tell how an ardent worker in science met his early death. For many years he enjoyed but indifferent health, which he attributed partly to the inhalation of chlorine when working at the Royal College of Chemistry, which occasioned hæmorrhage from the lungs, a complaint which would afterwards frequently return under the influence of any strong excitement, producing great depression and prostration of strength. His investigations at Marburg and elsewhere were interrupted from this cause. He had a serious illness after going to the factory in the Hartz, but shortly before his death he

said his health was better than it had been for some time, and that he was happier than he had supposed it possible he could be out of England. His early death makes serious deduction from the investigating power of this country. Chemical science can ill afford at the present moment to lose from her ranks an original investigator at once so active and so successful.

Mr. John Hunter, whose premature death has been greatly regretted by all who knew him, and in whom science has lost an ardent cultivator, was the only son of the late Dr. Hunter of Belfast, and belonged to a family long connected with the linen industry of the North of Ireland. He was born in Belfast on the 23rd of March, 1843, and being of a delicate frame of body, his early education was chiefly conducted under the parental roof. After passing with distinction through the Undergraduate course in Queen's College, Belfast, he graduated in 1863 with first class honours in the Queen's University in Ireland, and in the same year he gained the Senior Scholarship in Chemistry in the Belfast College. While holding this scholarship, he began his experiments on the absorbing power of charcoal for gases, and published his first paper on that subject. In 1865 he was made chemical assistant to the Professor of Chemistry, and in July, 1869, he formed one of the scientific staff in the Deep Sea Exploring Expedition under Dr. Carpenter and Dr. Wyville Thomson. In the following year he resigned his situation in Belfast, having been appointed to the Professorship of Mathematics and Natural Philosophy in King's College, Windsor, Nova Scotia. This situation he only held for one year, having suffered in health from the severity of the climate. On his return to this country he spent a few months in Scotland, and being advised to desist for some time from active work, he afterwards fixed his residence in the West of Ireland. His scientific ardour could not however be repressed, and he fitted up a laboratory and resumed his researches in his new abode. It was here he wrote his last scientific paper, which appeared in the Journal of this Society for August, 1872. This paper had scarcely been published, when his labours were brought to a premature end from an acute disease of the brain, of which he died at Enniscrone on the 13th September in the same year. Mr. Hunter was married in 1869, but has left no surviving children.

With the exception of his first paper, which appeared in the "Philosophical Magazine," all his scientific communications were made to this Society. His labours chiefly relate to the absorbing action of charcoal on gases and vapours, and have greatly extended our knowledge of this important subject. In his earlier experiments he examined the absorbing power of a large number of dense charcoals, chiefly for ammonia and carbonic acid. Having found that charcoal

prepared from the shell of the cocoa-nut exceeds all others in absorbing power, he used this charcoal in his subsequent experiments.

He made a very elaborate investigation of its action upon a large number of vapours at different temperatures, and among other results, he found that the relative amount of different vapours absorbed by charcoal varies with the temperature. Methylic alcohol, for example, is more largely absorbed than any other vapour between the temperatures of 90° and 127°, while the vapour of ordinary alcohol is more largely absorbed at 159° than that of methylic alcohol. In a later paper he examined the effect of pressure on the absorbing power of the charcoal.

Mr. Hunter's analyses of sea-water taken at various depths, from a few feet below the surface to the bottom of the Atlantic, by the Deep Sea Exploring Expedition of 1869, were first communicated to this Society. As regards the gases, the most remarkable result was a large increase in the amount of carbonic anhydride at low depths, while the nitrogen and oxygen were at the same time diminished. The saline constituents of the sea-water from different depths were tolerably constant, with the exception of a specimen which was in close contact with the bottom of the sea at a depth of 2,090 fathoms, in which a large excess of calcium salts was found.

Dr. Henry Beaumont Leeson was the son of a solicitor, and was born at Shirland Hall, Nottinghamshire, in 1803. After his school-days at Repton, he studied at Caius and Gonville College, Cambridge, where he took his A.M. degree, and assisted Professor Cuming in his chemical lectures. He was subsequently entered at Trinity Hall, Oxford, and passed the M.D. examination in 1840. He practised the profession of medicine in London, was placed on the staff of St. Thomas's Hospital, and obtained the fellowship of the Royal College of Physicians in 1847. He gave great attention both to technical chemistry and to the higher branches of natural philosophy, was one of the original members of our Chemical Society, and the Treasurer of the Cavendish Society. His name appears in the selected list of the Royal Society for 1849, he having declined to become a candidate for the F.R.S. till the mode of election was changed. He continued as Senior Physician, Governor, and Lecturer on Chemistry at St. Thomas's till 1853, when he retired to Bonchurch, in the Isle of Wight, and occupied himself mainly with his duties as a large landed proprietor and justice of the peace. His beautiful house and grounds were the resort, not merely of tourists, but of many visitors of European reputation. He was twice married, and he continued in good health and activity of mind till last autumn, when he died after an illness of but seven weeks' duration.

He was a gentleman of singularly original mind and considerable

learning, munificent and impulsive, with strong likings and aversions, and great tenacity of purpose. He was many-sided in his pursuits, and would throw his energy, sometimes into his professional or scientific studies, sometimes into Freemasonry (he was the Head of the 33rd degree, "the Most Puissant Sovereign Sir Knight Dr. Leeson"); metaphysical questions, theological studies, and landscape gardening would occupy his mind alternately, and late in life he took up astronomy and the deciphering of the Moabite stone. His lectures at St. Thomas's were illustrated with beautiful and costly apparatus, especially when he discoursed on light or electricity. Indeed, he invented many pieces of apparatus of service, especially in crystallography, electrotyping, and telegraphy by means of light-signals. Unfortunately, he had a great disinclination to sit down and write out his discoveries or his theories; and even his "System of Crystallography," announced as far back as 1854, has never been published; the plates, however, are in existence, as well as his fine collection of minerals; and his series of crystallographical models, which gained for him a Council Medal at the Great Exhibition of 1851, have been transferred, in accordance with his request, to the museum at Oxford. His principal contributions to our proceedings were—"On the Circular Polarisation of Fluids," "On Crystallography," and "On Isomorphism."

The leading thoughts of the system by which his name is best known, are thus explained by Mr. Samuel Highley:—"Dr. Leeson's method of treating crystallography was original, being founded on the observation of the natural growth of crystals and their physical characteristics, rather than on the usual purely mathematical method of treating this subject, and was intended to meet the practical requirements of chemical and mineralogical students, —in other words, 'the naturalist,' rather than the mathematician. His system may be thus summarised:—He considered that all crystal forms are referrible to four *equi-axed* crystallographic systems, viz.:—The 'RECTANGULAR,' with three axes at right angles to each other, as in fluor spar, characterised by *neutral* optical properties, with the exception of lamellar polarisation, in the case of alum, rock-salt, &c., and the unequal doubly refractive properties of cubazite, analcime, &c., due to unequal strain dependent upon the peculiar form of the trapezohedron, &c. The 'OBLIQUE,' with two axes at right angles and one 'oblique,' characterised, as in nitre, by *bi-axial* polarisation. The 'OBTUSE DOUBLY-OBLIQUE,' with all three axes oblique, and characterised by *uni-axial* polarisation, as in calcspar, and the 'ACUTE DOUBLY OBLIQUE,' with all three axes oblique, characterised by *circular* polarisation, as in quartz, amethyst, &c. Each of these four axe-systems was also characterised by other specific physical indications. Dr. Leeson further held that each of the four axe-systems possesses not only its

respective *prisms*, or, as he termed them, '*uni-secant*' forms (that is to say, each face cut *one* axis), but their respective *dodecahedrons* or '*bi-secant*' forms (in which each face cut *two* axes), and their respective *octohedrons*, or 'tri-secant' forms (in which each face cuts *three* axes). These are the holohedral forms; but by the enlargement of certain sets of faces at the expense of others, their *hemihedral* forms are produced. Each of the holohedral uni-, bi-, and tri-secant forms may have its faces multiplied, and so produce '*duplicate*' and '*re-duplicated*' forms, such as pyramidal-hexahedral, trapezohedral, triakisoctohedral, and tetracontahedral forms—all of which may have their hemihedral representatives. In fact, each prism contains *a series* of uni-, bi-, or tri-secant pyramids, their duplicate and re-duplicated forms, or their hemihedral representatives. Dr. Leeson considered that all elongated or *in-equi-axed* forms are entirely referrible to, and are actually produced by, the enlargement of certain sets of faces at the expense of others; also that many bodies occurred in twin or tesselated forms which are characterised by their optical properties. It may here be mentioned that the Rev. Walter Mitchell, the well-known crystallographer, has been (and quite independently) working in the same direction, and has arrived at very similar conclusions, opposed as they are to the existing theory of the orthodox six systems of crystallographic axes."

Frederick Muspratt was the third son of James Muspratt, Esq., of Seaforth Hall, near Liverpool. He was born in the year 1825. In 1843 he visited the University of Giessen, and after working for two years in Liebig's laboratory, returned home and became a partner in the alkali-works of Messrs. James Muspratt and Co., managing for a time the branch works at Newton. In the year 1848 he communicated to the Chemical Society the results of his elaborate analyses of Black-ash and Soda-ash, and in the following year, in conjunction with Mr. Joseph Dawson, contributed to our Journal a paper "on the Manufacture of Soda and on the Composition of Salt-cake, Black-ash, Soda-ash, and Soda-waste." In 1851 he retired from the business of manufacturing chemist and went out to Australia, where he contributed to the colonial journals several papers on the cultivation of the vine and the making of wine. Subsequently he returned to England and recommenced business as a manufacturing chemist at Widnes. He shortly afterwards withdrew from industrial pursuits and came to reside in London, where he died at the age of 47.

The late Alderman Robert Rumney, of Manchester, was born on the 9th November, 1812, at Leck, near Kirkby Lonsdale, where his father held a small farm which had been in the family for many

generations. The eldest of seven sons, Robert found that they were becoming, as he said, "too thick upon the land," and he accordingly took a situation as farm servant. At the age of 20, being out of work, he again, to use his own words, "took it into his head that he would go and see what was to be done in one of the large towns. And so, very much to the grief of his mother, he went out. He threw off his clogs and put on his Sunday 'shoon,'. and having found that there was a cart that conveyed butter all the way from the district to a town 70 or 80 miles off, he placed himself on that butter cart, and in about a couple of days found himself in that town." Thus entering Manchester with nothing but energy and strength, he ultimately became rich and respected, and only declined nomination to the mayoralty on account of failing health.

Taking a situation as a grocer's porter, he endeavoured in his scanty leisure to improve his education, which had been of the most elementary kind. He joined the Mechanics' Institute, and took out from the library a work on the Differential Calculus, an examination of which naturally convinced him that he had still very much to learn. He attended the classes held in the institution, and studied various branches of knowledge, including chemistry. The taste thus acquired for this science led him, after two or three changes, to begin business in a small way as a manufacturing chemist, and this was the germ of his subsequent commercial success.

As might be imagined, Mr. Rumney was very zealous in the pursuit and communication of knowledge. He became one of the most prominent directors of the Mechanics' Institution to which he owed so much of his own education, and he was an ardent advocate of all educational schemes for the benefit of his townsmen and the nation. His public work in this direction was both great and important. He was upon the governing bodies of Owens College and the Local School of Art, and a member of the Manchester School Board, as well as President of the Lancashire and Cheshire Association of Mechanics' Institutes. In the City Council too, his scientific knowledge made him a peculiarly valuable member of Gas, Water, and Health Committees.

At the suggestion of Dr. Lyon Playfair, Mr. Rumney prepared for the International Exhibition of 1862 a highly interesting collection of chemicals, &c., illustrating the improvements made in calico-printing and dyeing since the previous Exhibition of 1851. Among the business undertakings in which he had an interest, besides his own chemical works, was a large manufactory of paraffin oil near Chester.

Mr. Rumney was twice married, but left no children. He died on August 28, 1872, after a painful illness of some months' duration. A self-made man, he attributed his success to self-reliance and a capacity for self-denial, his favourite motto being "Trust in God and trust to

yourself." Earnest, guileless, generous, and kind, he will be long remembered by his townsmen for his private charities as well as for his public work.

Benjamin Charles Staples entered at an unusually early age the service of the eminent assayers and metallurgists, Messrs. Johnson and Matthey, and having shown an aptitude for figures, Mr. Percival Norton Johnson was not long in discovering his talent, and finding an employment suited to his taste in the assay offices connected with his business.

The young assayer found, with the growth of the business surrounding him, that much might be done to simplify the process of working out his results, for himself as well as for others of less arithmetical ability, and conceived the notion of tabulating his calculations, which had assumed the form of voluminous detail, in manuscript; these he re-arranged with peculiar accuracy, spending the leisure of some six or seven years in the laborious work, and the results were considered so trustworthy and of such value that, with the sanction of Messrs. Johnson and Matthey, he published them, and they now (as Staples' Tables) form the text-book of the assay offices generally in England, those of the Indian and Colonial Mints, and of most foreign establishments of eminence connected with the bullion trade.

After about 25 years' service with this firm, Mr. Staples was elected by them to fill a vacancy occurring in the assay office of the Goldsmiths' Company in January, 1864, which he retained until his premature death. His ability was there, as in his former sphere of work, duly appreciated, and the Court elected him a freeman of the Goldsmiths' Company without the usual fees.

He had been in bad health for some time prior to his death, and having been thrown out of a phaeton, sustained such a serious shock to his nervous system that he never recovered from it, and finally succumbed to the fatal malady of consumption on the 26th April, 1872, at the early age of 45 years.

Thomas Thomas, of Begbrook, Frenchay, near Bristol, who died on May 11th, 1872, aged 59 years, was one of the senior partners in the firm of Christopher Thomas and Brothers, Broad Plain Soap and Candle Works, Bristol. Born and brought up in the town of Llangadoch, Carmarthenshire, he had very few opportunities of mental cultivation beyond those of the ordinary private schools. When 17 years old, he removed to Bristol, whither his father and eldest brother had preceded him, to assist them in carrying on a small soap-boiling business. His active and penetrating mind soon perceived how empirical were the processes as then conducted, and how great was the

necessity for systematic knowledge. This he endeavoured to obtain by all the means in his power, which were but few, since the conduct of the business absorbed nearly the whole of his time. By dint of incessant perseverance, however, and undaunted by great difficulties, he succeeded in obtaining a considerable knowledge, not only of chemical facts, but also of the general laws of the science, which he was most successful in applying in his daily avocation. He collected all the standard works on chemistry, and in 1858 was elected a Fellow of the Chemical Society. He was rarely able to attend its meetings, but was a constant reader of its Journal, and a large contributor to any funds raised for special purposes in connection with it, *e.g.*, for the publication of the abstracts of foreign papers. Though not an original investigator, except in matters connected with his business, which developed very rapidly under his direction, he was keenly alive to the investigations of others, which he appreciated with the true spirit of the scientific man.

Of his private worth, of the estimation in which he was held in Bristol, and of his great amiability of character, this is perhaps not the place to speak. It is believed that the extreme mental activity of his earlier manhood laid the foundation of the disease of the heart which ultimately terminated his existence.

J. Chapman Wilson was born at Leeds in the year 1832. He was apprenticed to a chemist and druggist in that town, and availed himself of the special inducements of his calling for self-instruction in the elements of chemistry. He removed to London, and after a lapse of two or three years became connected with the weekly newspaper press.

This engagement afterwards led him to undertake the editorship of the *Cheshire Observer*, which he held for about two years. In the year 1860, Mr. Wilson took up an engagement more attractive to him than literary occupation, and more in accordance with his deeply-rooted love for chemistry. He became science master at the very large boys' school conducted by the late Mr. Dove, near Halifax. The curriculum was arranged so as to appeal to the practical ideas of manufacturers and others desiring that their sons should be trained with direct reference to the future callings for which they were destined. Large numbers of boys were daily instructed in practical chemistry and the applications of analysis, and many of these are now filling influential positions requiring chemical knowledge. Mr. Wilson was highly successful as a teacher, and continued this congenial occupation until the year 1865. He availed himself of the opportunity of passing a short session in the laboratory of the Pharmaceutical Society for the sake of some special work under the guidance of the director, Dr. Attfield. He then settled in his native town as an analytical chemist, and was soon

afterwards appointed Lecturer on Chemistry at the Leeds School of Medicine.

Mr. Wilson's last illness was the result of a misadventure. In the summer of 1869 he accompanied some friends in an excursion to the valley of the Wharfe, the party visiting the narrow gorge known as the Strid, not unfrequently crossed by a hazardous leap. In re-crossing, Mr. Wilson missed his footing, and narrowly escaped drowning; but the result of the submersion was disease of the lungs, which, after fluctuations that excited hope, ended fatally on November 1, 1872, in the forty-first year of his age.

Mr. Chapman Wilson was modest and unassuming, and free from all trace of censoriousness in his contact with others. His professional work was executed with a conscientious fidelity and accuracy that secured for him the confidence and esteem of both pupils and clients.

These are the losses which the closing year leaves us to deplore; but, on the other hand, your Council have to congratulate you, not only on the rapid increase in the aggregate number of your Fellows, but on what is of still more importance, the greatly increased number of original communications which have reached us during the past twelve months. At our last anniversary it was my painful duty to comment upon the diminishing energy with which chemical research was being prosecuted in this country, as exhibited by the diminishing number of communications contributed to the Society during the previous five years. I took occasion to remark that this phenomenon could not be attributed to the increasing difficulty of chemical research, because the progress of original investigation in other countries exhibited extraordinary activity. It is to be hoped that in our case this diminishing originality reached its lowest depression in the year 1871-72, when only 22 papers were presented to the Society. At all events it is gratifying to find that the year ending to-day exhibits a strong rebound from the lethargy of its predecessor, no fewer than 58 papers having been communicated to us by their authors since our last anniversary—a number which exceeds that received in any previous year of the Society's existence.

The following is a list of the papers read at our meetings from March 30th, 1872, to March 31st, 1873:—

I. "On Benzyl Isocyanate and Cyanurate:" by E. A. Letts.

II. "On a Compound of Sodium and Glycerin:" by E. A. Letts.

III. "On the Carbonic Acid in the Sea Water:" by Professor Himly.

IV. "On the Influence of Pressure on Fermentation," Part I.: by H. T. Brown.

V. " On the Electrolysis of Sugar Solutions:" by H. T. Brown.
VI. " On the Determination of the Solubility and Specific Gravity of certain Salts of Sodium and Potassium:" by D. Page and A. D. Keightley.
VII. "An Examination of a recent Attack upon the Atomic Theory:" by R. W. Atkinson.
VIII. " Notes from the Laboratory of the Andersonian University, Glasgow:" by Dr. T. E. Thorpe.
IX. " On the Transformation-products of Starch:" by C. O. Sullivan.
X. " On a Remarkable Salt Deposited from the Mother-liquors obtained in the Manufacture of Soda:" by Dr. E. T. Thorpe.
XI. On the Composition of Ceylon Jargons:" by M. H. Cochran.
XII. " On a Double Sulphide of Gold and Silver:" by M. Pattison Muir.
XIII. " On the Solvent Action of various Saline Solutions upon Lead:" by M. Pattison Muir.
XIV. " On the Magnetic Sand of Mount Etna:" by J. B. Hannay.
XV. " New Tests for some Organic Fluids:" by J. A. Wanklyn.
XVI. " Dendritic Spots on Paper:" by A. Liversidge.
XVII. " On Chinoline and Leucoline:" by C. G. Williams.
XVIII. " On some Derivatives of Chinoline:" by James Dewar.
XIX. " Action of Phosphoric Acid on Morphine:" by Dr. C. R. A. Wright.
XX. Note " On a Secondary Colouring Matter produced in the Preparation of Alizarin from Anthracene:" by W. H. Perkin, F.R.S.
XXI. " On the Effects of Temperature on the Absorption of Gases by Charcoal:" by John Hunter.
XXII. " On the Nitration-products of Dibromophenol-sulphonic Acids:" by Dr. H. E. Armstrong and F. D. Brown.
XXIII. " On Bromophenol-disulphonic Acid: its behaviour towards Nitric Acid and Bromine:" by Dr. H. E. Armstrong.
XXIV. " On the Formation of Substituted Nitrophenol-sulphonic Acids:" By Dr. H. E. Armstrong and F. D. Brown.
XXV. " On the Action of Charcoal on Organic Nitrogen:" by E. C. Stanford.
XXVI. " On Iona Pebbles:" by E. C. Stanford.
XXVII. "Mineralogical Notices:" by N. Storey-Maskelyne, F.R.S., and Dr. Flight.
XXVIII. " On the Specific Heat of Occluded Hydrogen:" by W Chandler Roberts and Dr. C. R. A. Wright.

XXIX. "On a Means of Preventing Explosions in Coal Mines:" by J. A. Newlands.

XXX. "On some Possible Reactions that yielded Negative Results:" by Dr. C. R. A. Wright.

XXXI. "On the Standardizing of Acids:" by W. N. Hartley.

XXXII. "On Anthraflavic Acid:" by W. H. Perkin, F.R.S.

XXXIII. "On the Hypophosphites:" by Professor C. Rammelsberg.

XXXIV. "On the Reducing power of Phosphorous and Hypophosphorous Acids and their Salts:" by Professor C. Rammelsberg.

XXXV. "New Analyses of certain Mineral Arsenates and Phosphates:" by Professor A. H. Church.

XXXVI. "On the condition of Hydrogen occluded by Palladium, as indicated by the Specific Heat of the charged Metal:" by W. Chandler Roberts and Dr. C. R. A. Wright.

XXXVII. "Analysis of the Water of the River Mahannddy:" by E. Nicholson.

XXXVIII. "Researches on the Polymerides of Morphine and their Derivatives:" by E. Ludwig Mayer and Dr. C. R. A. Wright.

XXXIX. "Communications from the Laboratory of the London Institution." No. 8. Derivatives of β-dinitrophenol.—No. 9. Action of Bromine in presence of Iodine on Trinitrophenol.—No. 10. Preliminary Notice on Iodo-nitrophenols: by Dr. H. E. Armstrong.

XL. "On the formation of Naphthaquinone by the direct Oxidation of Naphthalin:" by C. E. Groves.

XLI. "Notes on various Chemical Reactions:" by Mr. Davies.

XLII. "On Ethyl-amyl:" by Harry Grimshaw.

XLIII. "The Heptanes from Petroleum:" by Dr. Schorlemmer.

XLIV. "The Vanadates of Thallium:" by T. Carnelley.

XLV. "On the formation of Sodium Sulphide by the action of Hydrogen Sulphide upon Sodium Chloride at High Temperatures:" by T. Kingzett.

XLVI. "On the action of Sodium on Aniline:" by Dr. H. E. Armstrong.

XLVII. "On Anthrapurpurin:" by W. H. Perkin, F.R.S.

XLVIII. "Isomerism in the Terpene Family of Hydrocarbons:" by Dr. C. R. A. Wright.

XLIX. "On the Solidification of Nitrous Oxide:" by T. Wills.

L. "On Aurin:" by R. S. Dale and C. Schorlemmer, F.R.S.

LI. "Researches on the action of the Copper-zinc Couple on Organic Bodies. I. On Iodide of Ethyl:" by Dr. Gladstone, F.R S., and A. Tribe.

LII. "On the Detection of Ammonia in the Atmosphere:" by A. H. Smee, jun.

LIII. "Action of Hydrochloric Acid on Codeine:" by Dr. C. R. A. Wright.

LIV. "On a Method of Estimating Nitric Acid:" by T. E. Thorpe.

LV. "Note on a Reaction of the Acetates upon Lead Salts, with remarks on the Solubility of Lead Chloride:" by F. Field.

LVI. "Observations on the Nature of the Black Deposit in the Copper-zinc Couple:" by Dr. Gladstone and A. Tribe.

LVII. "On an Air-bath of constant Temperature between 100° and 200° C.:" by Dr. H. Sprengel.

LVIII. "On new Processes for Mercury Estimation, and some Observations on Mercury Salts:" by J. B. Hannay.

In addition to these original communications read at the meetings of the Society, we are indebted to our foreign Member, Professor Cannizzaro, and to four of our Fellows for lectures which excited great interest and attracted large audiences. The following are the titles of these discourses:—

1. "On the Chemistry of the Hydrocarbons:" by C. Schorlemmer, F.R.S.
2. "On the Manufacture of Iron and Steel:" by E. Riley, Esq.
3. The Faraday Lecture:—"Considerations on some points of the Theoretic Teaching of Chemistry:" by Professor Cannizzaro.
4. "On Deacon's Method of Obtaining Chlorine as Illustrating some Principles of Chemical Dynamics:" by H. Deacon, Esq.
5. "On Iron and Steel:" by C. W. Siemens, D.C.L., F.R.S.

The increased activity of British chemists in the prosecution of original research, as testified by the augmented number of papers communicated to the Society, is a most gratifying feature in the history of the past year, especially when the peculiar discouragements under which research labours in this country are taken into consideration. It must not be for a moment imagined, however, that we have in this important matter taken the position which we undoubtedly ought to occupy, as the nation holding the first place in wealth, trade, manufactures, and state revenue. The statistics of experimental discovery show that we are at present very far from the attainment of such a position. I have on a previous occasion expressed the opinion that the chief cause of this deplorable result is the non-recognition of experimental research by our universities. Further inquiries into the conditions under which degrees and honours in experimental science,

as given here and elsewhere, have only served to deepen my conviction that the progress of physics, chemistry, and biology is intimately bound up with the nature of the training prescribed by the governing bodies of universities for students of these sciences; and that, until a profound change is made in the awarding of prizes and the granting of degrees in science in this country, we shall look in vain for any substantial improvement in the prosecution of experimental investigation.

Under these circumstances it is very gratifying to find that the authorities of Trinity College, Cambridge, propose, at the Fellowship examination in 1874, to offer a Fellowship for adequate proficiency in natural science, to be tested not only by examinations, but by the deposition of any papers that the candidates may have published, containing original observations or experiments, or discussions of scientific questions, or any similar matter in manuscript. The papers must be accompanied by a statement as to what portions of the matter are claimed as original. It is announced that the examination will be chiefly in chemistry, physics, and biology, and it is understood that in awarding the Fellowship, great weight will be attached to the original dissertations sent in by the candidates. Such an innovation in the award of Fellowships will be followed with great interest by all who have the progress of scientific discovery at heart. Let us hope that it will inaugurate a new era in the university life of this country.

In conclusion, Gentlemen, having now completed the biennial period of service as your President, permit me, in surrendering this chair to my successor, to thank you most sincerely for the honor which you conferred upon me in electing me to that office. I feel strongly how imperfectly I have performed the functions of such a position; but my interest in the Society does not terminate with the vacation of this chair, and it is my earnest wish to be able, in a more humble capacity, to serve the Society more usefully than I have been able to do during the past two years.

The Treasurer then made his financial statement, after which the Society proceeded to the election of the Officers and Council for the ensuing year.

The following is a list of the Officers and Council:—

President.—W. Odling, M.B., F.R.S.

Vice-Presidents who have filled the office of President.—Sir B. C. Brodie, Bart., F.R.S.; Warren De la Rue, Ph.D., F.R.S.; E. Frankland, D.C.L., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.;

Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; Colonel P. Yorke, F.R.S.

Vice-Presidents.—H. Debus, Ph.D, F.R S.; A. Vernon Harcourt, M.A., F.R.S.; H. E. Roscoe, Ph.D., F.R S.; Maxwell Simpson, Ph D., F.R.S.; J. Stenhouse, LL.D., F.R.S.; A. Voelcker, Ph.D., F.R.S.

Other Members of the Council.—H. E. Armstrong, Ph.D.; A. Crum Brown, D.Sc.; Dugald Campbell; E. Divers, M.D.; B. F. Duppa, F.R.S.; A. Dupré, Ph.D.; G. C. Foster, F.R.S.; M. Foster, M.D., F.R.S.; H. McLeod; Peter Spence; Hermann Sprengel, Ph.D.; Thomas Stevenson, M.D.

Secretaries.—W. H. Perkin, F.R.S., and W. J. Russell, Ph.D., F.R.S.

Foreign Secretary.—H. Muller, Ph.D., F.R.S.

Treasurer.—F. A. Abel, F.R.S.

After the names of the Officers and Council for the ensuing year had been announced from the chair, votes of thanks were proposed to to the President, to the Officers and Council, to the Auditors, and to the Editor of the Journal and Abstractors.

Dr. The Treasurer in Account with the Chemical Society from March 25, 1872, to March 27, 1873. Cr.

Dr.	£ s d	£ s d
Balance in hand March 25th 1872		1084 14 7
Dividends on £3000 Consols		88 10 0
Sale of Journals by Publisher		183 16 7
Receipts by Subscription and Fees from 8th March 1872, to 8th March 1873		
12 Life Compositions	240 0 0	
76 Admission Fees	152 0 0	
8 Subscriptions for 1869	6 0 0	
8 " " 1870	16 0 0	
16 " " 1871	32 0 0	
150 " " 1872	281 0 0	
335 " " 1873	648 0 0	
		1375 0 0
Excess payments on subscriptions		0 6 6
Donation from J. Hyde Hills, Esq., towards fund for promoting original research		10 10 0
Monthly Report Fund		
Subscriptions for 1872		257 17 0
		£3450 14 8

Assets	£ s d
Balance at Messrs. Coutts	1941 18 9
Three per Cent. Consols	3000 0 0

Cr.	£ s d	£ s d
Expenses on Account of the Journal		
Editor's Salary, 9 months at £150, 3 months at £200	162 10 0	
Fees paid for Abstracts of Papers	155 5 0	
Periodicals required for preparation of Abstracts	24 13 0	
Editor for Translations and incidental expenses	3 10 0	
Printing of Journal	551 0 3	
Distribution of Journals, and of Proceedings of the Royal Society	113 5 6	
		1016 9 9
Printing of Authors' Copies of Papers and Miscellaneous Printing		[illegible]5 [illegible] 0
Supply of Proceedings of the Royal Society to Fellows		100 0 0
Preparation of Reports of Proceedings at the Meetings		[illegible] 0 0
Stationery and Postage Envelopes		16 3 0
Expenses on Account of Library		
Salary of Librarian	25 0 0	
Salary of Library Attendant	52 0 0	
Books and Periodicals	[illegible] 12 6	
Binding Books and Periodicals	13 4 6	
		112 17 0
Expenses on Account of Faraday Lecture		
Gratuity to the Faraday Lecturer	20 0 0	
L. C. Wyon for copy of Faraday Medal and Case and Preparation of Palladium impressions	8 1 0	
Printing of Circulars and Lecture Cards	3 8 7	
		31 9 7
Grants in aid of original research		30 0 0
Collector's Commission on Subscriptions		68 15 0
Return of excess payments on subscriptions		0 6 6
Treasurer's Stamps, Postage and Clerical Expenses and Draft Stamps		12 9 6
Messrs. Banks and Barry for Plans of New Premises		4 4 0
House Expenses		
Provision of Tea at Meetings	24 17 9	
Coals	4 9 0	
Gas and Lamps for Meeting Rooms	12 9 0	
Gratuities to House Porter and Hall Porter	7 2 0	
Cleaning of Meeting Room and Library	6 14 0	
Petty Expenses	10 6 7	
		65 18 4
Balance at Messrs. Coutts		1941 18 9
		£3450 14 8

April 3, 1873.

Professor Odling, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

E. H. Fison; C. T. Kingzett; Alonzo J. Rider; Roland Finch; William Morgan; Henry Richardson; William Andrew Prout.

The following papers were read:—

"On a Method of Determining the Specific Gravity of Liquids with ease and great exactness:" by H. Sprengel.

"Researches on the Action of the Copper-zinc Couple on Organic Bodies. No. II. On the Iodides of Amyl and Methyl:" by J. H. Gladstone and A. Tribe.

"On Cymenes from Various Sources:" by C. R. A. Wright.

"Action of the Acid Chlorides on Nitrites and Nitrates:" Part I— "Action of Acetic Chloride:" by H. E. Armstrong.

April 17, 1873.

Professor Odling, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

James Hughes; Henry Tylston Hodgson.

Dr. Debus delivered a lecture on the "Heat produced by Chemical Action."

May 1, 1873.

Professor Odling, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Isidore Bernadotte Lyon; John Henry Baldock.

The following papers were read:—

"On a New Class of Explosives:" by H. Sprengel.

"On Zirconia:" by J. B. Hannay.

"A Note on Pyrogallate of Lead and on Lead Salts:" by W. H. Deering.

May 15, 1873.

Professor Odling, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

William Henry Greenwood; Walter Hills.

Dr. H. E. Armstrong delivered a lecture on "Isomerism."

June 5, 1873.

Professor Odling, President, in the Chair.

The following papers were read:—

"On the Dioxides of Calcium and Strontium:" by Sir John Conroy, Bart.

"A New Ozone Generator:" by T. Wills.

"On the Behaviour of Acetamide with Sodium-alcohol:" by W. Hartley.

"On Iodine Monochloride:" by J. B. Hannay.

"On Triferrous Phosphide:" by Dr. Schenk.

"On Sulphur Bromide:" by J. B. Hannay.

June 19, 1873.

Professor Odling, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

Archibald Kitchin; Walter Odling; James Emmerson Reynolds; Robert Wild.

The following papers were read:—

"Researches on the Action of the Copper-zinc Couple on Organic Bodies. III. On Normal and Isopropyl Iodides:" by J. H. Gladstone and A. Tribe.

"On the Influence of Pressure on Fermentation. Part II. The Influence of Reduced Pressure on the Alcoholic Formentation:" by Horace T. Brown.

"On Cymene from different sources optically considered:" by J. H. Gladstone.

"Note on the Action of Bromine on Alizarin:" by W. H. Perkin.

"On some Oxidation and Decomposition Products of Morphine Derivatives:" by E. L. Mayer and C. R. A. Wright.

"On the Decomposition of Tricalcic Phosphate by Water:" by R. Warington.

"On the Nature of some Derivatives of Coal-tar Cresol:" by H. E. Armstrong and S. Field.

"On a New Tellurium Mineral, with Notes on a Systematic Mineralogical Nomenclature:" by J. B. Hannay.

"Note on a Relation among the Atomic Weights:" by J. A. R. Newlands.

Donations to the Library. Session 1872–73.

"The Royal Society's Catalogue of Scientific Papers," Vol. VI.: from the Royal Society.

"Michael Faraday": by Dr. J. H. Gladstone: from the Author.

"A Manual of Metallurgy:" by G. H. Makins: from the Author.

"Mineral Phosphates and Pure Fertilizers:" by Dr. Campbell Morfitt: from the Author.

"Memoir of Sir Benjamin Thompson, Count Rumford, with Notices of his Daughter:" by George E Ellis: from the American Academy of Arts and Sciences at Boston.

"The complete Works of Count Rumford," published by the American Academy of Arts and Sciences at Boston: from the Academy.

"Traité des Dérivés de la Houille, applicables à la production des Matières colorantes:" par E. Girard et G. de Laire: from the Authors.

"Sur les Dérivés acides de la Naphtylamine:" par D. Tommasi: from the Author.

"Notices Chimiques et Cristallographiques de quelques Sels de la Glucine et des Métaux de la Cérite:" par C. Marignac: from the Author.

"Observations sur les Critiques dont le Calorimètre-à-mercure a été l'objet:" par P. A. Favre: from the Author.

"Sursaturation:" par C. Tomlinson: traduit de l'Anglais sous la direction de M. l'Abbé Moigno: from the Abbé Moigno.

"Centième Anniversaire de l'Académie Royale de Belgique:" 2 Tomes: from the Academy.

"Die Aufgabe des chemischen Unterrichts mit Bezug auf die Forderungen der Wissenschaft und der Praxis:" von E. Erlenmeyer: from the Royal Bavarian Academy of Sciences.

Periodicals:—

"Philosophical Transactions" for 1872: from the Royal Society.

"List of Officers and Fellows of the Royal Society for 1872:" from the Royal Society.

"Quarterly Journal of Science," 1872–73: from the Editor.

"Pharmaceutical Journal and Transactions," Third Series, Vol. III: from the Pharmaceutical Society.

"Journal of the Society of Arts," 1872–73: from the Society.

"Chemical News," 1872–73: from the Editor.

"The Photographic Journal," 1872–73: from the Photographic Society.

"Memoirs of the Royal Astronomical Society," Vol. XXXIX., Part II (1871–72): from the Society.

"Monthly Notices of the Royal Astronomical Society," 1872–73: from the Society.

"Annual Report of the Council of the Royal Astronomical Society for 1872:" from the Society.

"Quarterly Journal of the Geological Society," 1872–73: from the Society.

"Nature," 1872–73: from the Editor.

"Year-book of Pharmacy," 1872: from Professor Attfield.

"Proceedings of the Royal Institution of Great Britain," Vol. VII, Part I: from the Institution.

"The Practical Magazine," Nos. 1, 2, 3: from the Editor.

"The Telegraphic Journal," Nos. 1 and 2: from the Editor.

"Report of the Royal Cornwall Polytechnic Society for 1872:" from the Society.

"Communications to the Monthly Meetings of the Yorkshire Philosophical Society, 1872:" from the Society.

"The Canadian Journal," December, 1872: from the Canadian Institute.

"Proceedings of the Academy of Natural Sciences at Philadelphia," 1872: from the Academy.

"Proceedings of the American Philosophical Society," July to December, 1872: from the Society.

"Third and Fourth Annual Reports of the Geological Survey of Indiana, made during the years 1871 and 1872:" by E. T. Cox, State Geologist: from the State of Indiana.

"The American Chemist," 1872–73: from the Editor.

"Les Mondes," 1873: from the Editor.

"Revue Scientifique," Nos. 27, 28: from the Editor.

"Bulletin de l'Académie Royale de Belgique," Tomes xxxi—xxxiv (1871–72): from the Academy.

"Annuaire de l'Académie Royale de Belgique." 1872 et 1873: from the Academy.

"Memorie dell' Accademia delle Scienze dell' Istituto di Bologna," Serie 3, Tomo I, e Tomo II, Fascicolo 1: from the Academy.

"Rendiconti dell' Accademia delle Scienze dell' Istituto di Bologna," 1871—72: from the Academy.

"Giornale di Scienze naturali ed economiche dell' Istituto tecnico di Palermo," Tomo II, Fascicolo 1: from the Institute.

"Berichte der deutschen Chemischen Gesellschaft zu Berlin," 1872—73: from the Society.

"Denkschriften der Kaiserlichen Akademie der Wissenschaften (mathematisch-naturwissenschaftliche Klasse)," 31ter and 32ter Band.

"Sitzungsberichte der Kaiserlichen Akademie der Wissenschaften

(mathematisch-naturwissenschaftliche Klasse), Erste Abtheilung 64ter Band, Zweite Abtheilung 64ter und 65ter Band

"Register zu den Bänden 56—64 der Sitzungsberichte" from the Imperial Academy of Sciences at Vienna

"Abhandlungen der Koniglich bayerischen Akademie der Wissenschaften (mathematisch naturwissenschaftliche Klasse)," 11ter Band Erster Theil from the Academy

"Verhandlungen der physikalisch-medicinischen Gesellschaft zu Erlangen," 4ter Theil from the Society

"Vierteljahrschrift der naturforschenden Gesellschaft in Zurich 16ter Band from the Society

"Kongl Vetenskaps Akademiens Handlingar," 1868, 1869, and 1870 from the Royal Academy of Sciences at Stockholm

"Ofversigt af Kongl Vetenskaps Akademiens Forhandlingar," 1869, 1870 from the Royal Academy of Sciences at Stockholm

"Journal of the Russian Chemical Society," 1873, Nos 1—5 from the Society

"Proceedings of the Medico Philosophical Society of Amsterdam," 1871—72 from the Society

"Bulletin of the Chemical Society of Prague," Parts 1 and 2 from the Society

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXXII.—*On a New Class of Explosives which are Non-explosive during their Manufacture, Storage, and Transport.*

By HERMANN SPRENGEL, Dr. phil.

MR. ALFRED NOBEL'S important discovery of effecting the explosion of "nitroglycerin and other analogous substances"* by detonation, or (to quote his own words† of 1864), "The detonation of explosive bodies, either non-inflammable, or which may be ignited without explosion by spontaneous decomposition of a small portion of their mass, thus producing an initiative explosion, which spreads of itself," instituted a new era in the history of explosives.

The detonation of nitroglycerin in the form of dynamite, "under all conditions of confinement or non-confinement, by means of a strong fulminating cap,"‡ by the same discoverer in 1867, who then stated that "the principle for its action lay in the sudden development of a very intense pressure or shock;"§ the happy application of this principle by Messrs. Abel and Brown in 1868, to the detonation of "gunpowder, gun-cotton, and other explosive compounds (excepting nitroglycerin and dynamite), when in an unconfined state,"‖ and my own experiments with their results¶ in 1871, may all be regarded as the natural development of Mr. Nobel's first discovery.

The views which guided me in making these experiments were the following:—

A shell, containing common air, may be made to explode, either by placing it in a vacuum or in a heated chamber, under the ordinary atmospheric pressure, provided that the difference of pressure thus established is greater than the resistance of the shell. If we adopted means of firing a cannon inside a room the atmosphere of which was as dense as the gases generated by the combustion of the gunpowder, no explosion (properly speaking) could ensue, and the projectile would remain at rest.

This illustrates that an *explosion* is the sudden release of that force which kept together or compressed the molecules of gaseous matter, ever ready to repel and disperse each other to an almost infinite

* Vide A. Nobel's English patent, No. 1813, July 20th, 1864. † Ibid.

‡ Vide A. Nobel's English patent, No. 1345, May 7th, 1867. § Ibid.

‖ Vide F. A. Abel and E. O. Brown's English patent, No. 3115, October 10th, 1868.

¶ Vide H. Sprengel's English patents, No. 921, April 6th, 1871, and No. 2642, October 5th, 1871.

degree.* Both the solid and liquid state of matter may be viewed as the limit of this compressibility, and *explosives* are those solids and liquids which can be made to assume suddenly the gaseous state. Heat, or arrested motion transformed into heat appears, as a rule, to be the cause of these sudden decompositions, which in most cases are simply *sudden combustions* of compounds arranged so that the products of combustion shall be gaseous either wholly or in part. Still we are acquainted with a variety of highly explosive compounds, which contain either so little oxygen that their explosiveness can hardly be attributed to sudden combustion as the only reason (such as Howard's fulminating mercury, $C_2Hg(NO_2)N$, Brodie's peroxide of acetyl, $C_4H_6O_4$, Berthelot's acetylene copper $(C_2HCu_2)_2O$, Griess's nitrate of diazobenzene, $C_6H_4N_2.HNO_3$, &c.), or which contain no oxygen at all (such as Dulong's chloride of nitrogen, Cl_3N, iodide of nitrogen, I_2HN, &c.). An explosion, like that of iodide of nitrogen, started by the gentle touch of a feather, may be viewed as similar to the tumultuous boiling over of a superheated liquid, seemingly produced by a grain of sand thrown into it. Iodide of nitrogen and its congeners ought to be gaseous at common temperatures. At any rate, the fettered tension existing in one or more of their gaseous constituents, suddenly exerts itself, and the cause which loosened this bond seems to be, in most cases, heat or arrested motion.

The relative volume of gas thus formed, depends, in the first instance, on the total or partial gasification of the explosive, and in the second on the degree of temperature imparted to the same. Taking 0·003665 as the average expansion-coefficient of gas, an increase of every 273° C. will effect an expansion in the volume equal to the total amount of the evolved gas when measured at 0°. Hence it is quite the same, as far as regards the pressure, whether an explosive evolves a greater amount of gas and less heat, or proportionally a smaller amount of gas and more heat. Both the amount and the degree of heat generated by these sudden combustions, depend to a not inconsiderable extent on the chemical composition of the combustible, and may, in this way, be raised or lowered, *e.g.*, in burning by the same weight of oxygen hydrocarbons differing in composition.† Still the maximum of heat, both in amount and in degree, which is conceivable, cannot be attained in practice, on account of our inability to supply pure or elementary oxygen in either a solid or a liquid form. We are, therefore, compelled to have recourse to a form in which it is combined already with another element or with a group of elements, but combined so loosely that their mutual adhesion may suddenly be suspended by an initiative explosion in the presence of hydrogen or carbon, which elements, for the sake of their cheapness

* Vide H. Sprengel's Researches on the Vacuum (*Journ. Chem. Soc.*, [2], iii, p. 20, 1865).

† Vide Bunsen's *Gasometrische Methoden; Verbrennungserscheinungen der Gase.*

and on account of their yielding the least obnoxious products of oxidation, are, for practical purposes, the most suitable combustibles that can be employed. These vehicles of oxygen, however, even when themselves gaseous after combustion, are objectionable because they are seldom generators of heat, and thus cool the other products of combustion. The potential energy resulting from such a chemical reaction appears mainly to depend on the suddenness of the combustion: on the varying proportions of hydrogen and carbon in the hydrocarbons, which may be employed; on the density or specific gravity of the explosive thus formed; and especially on *the amount of oxygen available* for the conversion of hydrogen and carbon into water and carbonic acid.

A survey of oxygen-compounds (more or less connected with this subject) led to the following table, which shows the total amount of oxygen they contain, and the oxygen available for combustion:

Name.	Formula.	Total O in 100.	Available O in 100.
Peroxide of hydrogen	H_2O_2	94·1	47·0
Water	H_2O	88·8	—
Nitric acid	HNO_3	76·2	63·5
Nitric anhydride	N_2O_5	74·0	74·0
Carbonic acid	CO_2	72·7	—
Peroxide of lithium ?	Li_2O_2	71·1	35·5
Oxalic acid	$H_2C_2O_4$	71·1	—
Nitric peroxide	NO_2	69·5	69·5
Tetranitromethane	$C(NO_2)_4$	65·3	65·3
Sulphuric acid	H_2SO_4	65·3	?
Perchloric acid	$HClO_4$	63·6	55·7
Trinitroglycerin	$C_3H_5(NO_2)_3O_3$	63·4	42·3 ?
Nitrate of ammonia	NH_4NO_3	60·0	50·0 ?
Gun cotton	$C_6H_7(NO_2)_3O_5$	59·3	32·3 ?
Nitrate of sodium	$NaNO_3$	56·4	47·0
Trinitroacetonitril	$C_2(NO_2)_3N$	54·5	54·5
Peroxide of acetyl	$C_4H_6O_4$	54·2	13·5 ?
Acetic acid	$C_2H_4O_2$	53·3	?
Glycerin	$C_3H_8O_3$	52·2	?
Silica	SiO_2	51·9	—
Nitrate of urea	H_4N_2CO,HNO_3	51·4	32·5
Cellulose	$C_6H_{10}O_5$	49·4	?
Picric acid	$C_6H_3(NO_2)_3O$	48·9	41·9
Nitrate of potassium	$KaNO_3$	47·5	39·6
Chlorate of potassium	$KaClO_3$	39·2	39·2
Cyanic acid	$CNHO$		
Cyanuric acid	$C_3N_3H_3O_3$	37·2	?
Cyamelide	$C_nN_nH_nO_n$		
Fulminuric acid	$C_3H_3N_3O_3$		
Peroxide of manganese	MnO_2	36·7	18·3
Nitrate of diazobenzene	$C_6H_4N_2,HNO_3$	28·7	23·9
Nitrobenzene	$C_6H_5(NO_2)$	26·2	26·2
Iodic acid	I_2O_5	23·9	23·9
Phenol	C_6H_6O	17·1	?
Fulminating mercury	$C_2Hg(NO_2)N$	11·2	11·2
Charcoal	$C_mH_nO_p$	10·0	?

This table illustrates that the total amount of oxygen in a compound is by no means a criterion of the amount available for combustion. To decide upon this amount is in some cases a matter of doubt, especially when we have to consider the availableness of the constitutional oxygen in organic compounds, such as in cellulose, glycerin, acetic acid, charcoal, &c., or when we have to face cases of isomerism, such as are represented by cyanuric and fulminuric acid. Does the oxygen in them, or a portion of it, take part in the combustion? If the explosion of gun-cotton and nitroglycerin is merely the sudden combustion of carbon and hydrogen at the expense of the oxygen, supplied by the three molecules of nitric peroxide, *mixtures* may be formed which contain (with reference to the foregoing table) more available oxygen than these powerful explosives, and therefore ought to surpass them in effect.

Led by the idea that (as a rule), an explosion is a sudden combustion, I have submitted a variety of mixtures of oxidising and combustible agents to the violent shock of a detonating cap. These mixtures were made in such proportions, that their mutual oxidation and deoxidation should be theoretically complete.

In all my experiments, I used that form of percussion cap which has been described in Messrs. Abel and Brown's patent, and consists in a conical metallic tube of about the size of a goose-quill 5·6 cm. ($2\frac{1}{4}''$) long, and containing 0·65 gram (10 grains) of fulminating mercury. Such a cap was pushed over the end of a slow-match or miner's safety-fuse, and the capped end, in some cases free, in others surrounded by a *thin* glass tube 10 cm. (4″) long and sealed at the end, was then placed in the middle of the mixture expected to be explosive. By igniting the other end of the fuse, the fulminate was made to detonate, to shatter its envelopes, and to spend its energy upon the explosive mixture, which was placed in an open, wide-mouthed glass-bottle, containing from 20 to 100 grams at a time.

On referring to the foregoing table, the reader will be reminded that peroxide of hydrogen is the highest oxygen-compound known, while nitric anhydride is the compound which contains the largest amount of oxygen available for combustion. But as this compound, as well as the next two, nitric peroxide and tetranitromethane are, at present, on account of their nature and their difficult preparation, mere chemical curiosities, my attention naturally turned to the fourth, to *nitric acid*, which is a cheap and common article of commerce. Thus I found that (subject to certain conditions), *a variety of organic substances dissolved in nitric acid of about* 1·5 *sp. gr., explode by detonation.*

Hydrocarbons afford us the most suitable combustible agents that can be dissolved; but as their solution in nitric acid is attended with

a violent chemical reaction and a considerable evolution of heat, owing to the formation of nitro-compounds, it is preferable to dissolve these nitro-compounds themselves. Phenol, for instance, when incautiously added to nitric acid, raises the temperature of the mixture to the point of ignition, while trinitro-phenol used in its stead, lowers the temperature so considerably, that the two may be used as a very effective freezing-mixture.

Most instructive is a study of the elementary composition of these mixtures compared side-by-side with that of known explosives, such as gun-cotton and nitroglycerin. Here follow a few:—

1. Nitrobenzene, $C_6H\,(NO_2)$ = 28·08
Nitric acid, $5(HNO_3)$ = 71·92
100·00

Elementary composition before explosion.		Supposed composition after explosion.	
C .... =	16·44	CO_2 ...... =	60·27
H ...... =	2·28	H_2O .... =	20·55
N ...... =	19·18	N .... =	19·18
O .... =	62·10		100·00
	100·00		

2. Trinitrophenol, $C_6H_3(NO_2)_3O$ = 58·3
Nitric acid, $2\frac{2}{3}(HNO_3)$ .... = 41·7
100·0

Elementary composition before explosion.		Supposed composition after explosion.	
C .... =	18·33	CO_2 ...... =	67·20
H .... =	1·43	H_2O ...... =	12·83
N .... =	19·97	N .... =	19·97
O .... =	60·27		100·00
	100·00		

3. Gun-cotton, $C_6H_7(NO_2)_3O_5$.

Elementary composition before explosion.		Supposed composition after explosion.	
C .... =	24·24	CO_2 ...... =	55·52
H .... =	2·36	H_2O ...... =	21·24
N .... =	14·14	N .... =	14·14
O .... =	59·26	C .... =	9·10
	100·00		100·00

4. Trinitroglycerin, $C_3H_5(NO_2)_3O_3$.

Elementary composition before explosion.		Supposed composition after explosion.	
C........=	15·85	CO_2......=	58·18
H.. .....=	2·20	H_2O.. ...=	19·80
N........=	18·50	N........=	18·50
O........=	63·45	O........=	3·52
	100·00		100·00

These analyses show that my mixtures leave no useless remnants, no carbon as in gun-cotton, no oxygen as in nitroglycerin, though of course the decompositions are actually not so simple as represented here. But it is evident that the elementary composition of mixtures can be modified, while that of chemical compounds is unalterable and rigid. By increasing or decreasing the weight of the hydrocarbon, we may utilise all available oxygen and produce either carbonic oxide or carbonic acid, or a mixture of both, in other words, we may produce more gas and less heat or less gas and more heat, as in common gunpowder, by means of altering the proportion of charcoal.

The *nitrobenzene mixture* of the above composition explodes with intense violence if fired by a detonating fuse. Nitrobenzene is freely soluble in nitric acid, from which it separates again when diluted with water to about 1·42 sp. gr. Some heat is evolved at the beginning of the mixing; hence larger quantities require to be cooled. I noticed a rise to 50° in mixing 25 c.c. Dinitrobenzene would probably lower the temperature. The mixture has the appearance of nitric acid, though the addition of 28 per cent. of nitrobenzene seems to render the acid less volatile and less hygroscopic. When incorporated with infusorial earth, it burns with a pale flame like dynamite, but less briskly. No sign of explosiveness was noticed while burning. I found it very difficult to effect its explosion by concussion when small pellets of the plastic mass, wrapt up in tinfoil, were placed on an anvil. Gun-cotton and Nobel's dynamites treated in a like manner exploded on a far lighter blow. The explosion of 35 grams of the liquid, contained in an open glass bottle, which was placed on a plate of wrought-iron 6·5 mm. ($\frac{1}{4}''$) thick, produced a deep and fractured indent, while the explosion of a disc of compressed gun-cotton (35 grams), placed on another part of the same plate, produced an indent less deep and not fractured. The same quantities (35 grams) of the nitrobenzene mixture, of gun-cotton and of nitroglycerin, exploded on planks of pine-wood, 7·6 cm. (3″) thick, produced in all three cases pretty nearly the same effects. The wood became perforated and splintered. It is to be regretted that

no exact method yet exists for comparing the force of detonating explosives.

The following considerations lead me to think that my acid explosives ought to surpass in force any others hitherto known.

Since we have to regard five equivalents of oxygen in the nitrobenzene-mixture as unavailable, or as united already with the hydrogen of the nitric acid in the form of water, and since we may regard in a like sense three equivalents of oxygen in nitroglycerin, viz., that derived from the glycerin (a triatomic alcohol), we find that in the nitrobenzene-mixture there remain 52·97 per cent., in the nitroglycerin 42·3 per cent. of oxygen available for combustion, of which, however, only 38·77 per cent. can be utilised for want of fuel. As potential energy stands in correlation to heat evolved and oxygen consumed during a combustion, I am perhaps justified in regarding the above figures as a rude measure of force for these two explosives. Consequently, I expect that the force of nitroglycerin will be to that of nitrobenzene acid—

as 38·77 to 52·97, or
as 100 to 136·6.

In taking 1 equivalent or 2 parts by weight of binitrobenzene and 4 equivalents or 3 parts by weight of nitric acid, the available oxygen of the mixture rises to 53·3 per cent.

How this or any of the following mixtures behave when kept mixed for a length of time I am unable to state, as I always exploded them soon after mixing. A small addition of water seems to destroy their explosiveness. At least I failed under the above conditions to explode the nitrobenzene-mixture, when the nitric acid contained less than 95 per cent. of the monohydrate. Confinement of the charge and a stronger fulminating cap might perhaps allow a greater dilution with water. The high specific and latent heat of water, absorbing the initial heat, which is evolved by the explosion of the detonator, may be the explanation of this non-explosiveness. I cannot help connecting the remarkable explosiveness of fulminating mercury with the fact that the specific heat of mercury is 30 times less than that of water. Fulminating mercury contains 70 per cent. of mercury.

Bunsen (*Gasometrische Methoden*, p. 258) diluting by degrees explosive gas-mixtures with incombustible ones, made the observation that the explosiveness of the mixed gases suddenly ceased at a very sharp limit.

Picric acid (58·3 parts) is freely soluble in an equivalent quantity of nitric acid (41·7 parts). During solution (as mentioned before), the temperature sinks so low, that the glass in which the mixing is made

soon becomes frosted. Like the former mixture, it explodes with very great violence when fired by a detonator.

Excluding one-sixth of the oxygen of the nitric acid, and likewise the oxygen, derived from the phenol, there remain 50·92 per cent. available for combustion.

Be it noticed here that picric acid alone contains a sufficient amount of available oxygen to render it, without the help of foreign oxidisers, a powerful explosive when fired by a detonator. Its explosion is almost unaccompanied by smoke.

In evidence of the intense heat which is generated by the combustion of these mixtures, I may relate the following fact:—A machine-pressed cartridge, made of brass, having a length of 4·8 cm., a diameter of 1·3 cm., and a weight of 11·4 grams, was charged partly with sporting powder (0·65 gram, or 10 grains), partly with 1·3 gram (20 grains) of sand, moistened with (scarcely 0·65 gram) of the above nitro-picric acid, the sand resting on the powder. The cartridge with a bullet was then introduced without delay into the cold barrel of a breech-loading Martini-Henry rifle and discharged. On extracting the case, the upper half of it was found to have completely lost its shape. It had become melted, while particles of sand, which had been retained in the cartridge, appeared to be fused together as if struck by lightning.

It is obvious that a great variety of combustible agents may be used in place of the two above mentioned. Though it is preferable for the sake of a thorough mixture, that a complete solution should take place, this does not appear to be absolutely necessary, as I succeeded in exploding a mixture which was made by adding—

17·4 parts of naphthalene to about
82·6 „ nitric acid

100·0

The mixture thus formed is semi-fluid in consequence of holding in suspension a micro-crystalline precipitate.

The same reason which led to the use of nitro-benzene in preference to benzene, suggests the use of partially oxidised compounds from the alcohol and fatty acid series. I regret that on this point I have not any trustworthy experiments to offer.

An aceto-nitric acid mixture would have to consist of—

Acetic acid $C_2H_4O_2$........... = 37·3
Nitric acid $1\frac{2}{3}(HNO_3)$ .... = 62·7

100·0

Elementary composition before explosion.		Supposed composition after explosion.	
C........ =	14·92	CO_2...... =	54·84
H. ...... =	3·47	H_2O...... =	31·23
N........ =	13·93	N........ =	13·93
O........ =	67·63		
	100·00		100·00

Should a mixture of nitric and acetic acid prove to be non-explosive, it would be an interesting piece of evidence in favour of the importance of the molecular arrangement in an explosive compound. Be it remembered, that Brodie's peroxide of acetyl (*Phil. Trans.*, cliii, 1863) is one of the most violent explosives known. The composition and near relationship of acetic acid (1) and peroxide of acetyl (2) :—

(1.) $\left.\begin{matrix} C_2H_3O \\ H \end{matrix}\right\} O$		(2.) $\left.\begin{matrix} C_2H_3O \\ C_2H_3O \end{matrix}\right\} O_2$	
C.... =	40·0	C .... =	40·7
H.... =	6·6	H.... =	5·0
O.... =	53·4	O.... =	54·3
	100·0		100·0

leads one to expect that a mechanical admixture of available oxygen would impart to acetic acid the explosiveness of its peroxidised radical.

The choice of oxidising agents is far more limited than that of combustible ones, especially when we require a perfect gasification of the compound. Among these *ammonium nitrate* (NH_4NO_3) is the next that ought to arrest our attention, as it is composed of—

N .... =	35	corresponding to	N.... =	35
H.... =	5		H_2O.. =	45
O .... =	60		O.... =	20
	100			100

It is to be regretted that this substance is hygroscopic, otherwise it might be used with advantage as an admixture to or as a substitute for potassium nitrate in common gunpowder. Air-tight cartridges and an incorporation with a non-volatile hydrocarbon as fuel for those 20 per cent. of oxygen, which are not claimed by the hydrogen of the ammonium, would meet this difficulty.

I found that an admixture of ammonium-nitrate to sporting powder increased the initial velocity of projectiles as follows:—

Weight of sporting powder.	Weight of NH_4NO_3 powder.	Weight of bullet.	Initial velocity per second.
4·92 gram.	—	31·49 gram	410 m.
3·69 "	+ 1·23 gram (*a*)	31·49 "	431·5 m.
2·46 "	+ 2·46 " (*b*)	31·49 "	452·2 m.

(a) consisted of 100 NH_4NO_3 + 7·5 lamp-black
(b) " 80 " + 15 dogwood-charcoal.

The ammonia-powder was mixed (before being put into the cartridge) with the sporting powder, of which a small portion had been retained to surround the percussion cap. The velocities of the bullets were determined by means of Le Boulengé's chronograph.

In substituting nitrate of urea (mixed with saltpetre) for its congener nitrate of ammonia, I perceived no acceleration of the bullet. Nitrate of urea, be it remembered, contains no water of crystallisation and is a perfectly stable and non-hygroscopic salt.

Nitroglycerin may be regarded as another oxidising agent of complete gasification. Containing as it does an excess of 3·52 per cent. of oxygen, it has been proposed elsewhere* to utilise this oxygen by adding the proper equivalent of fuel. Thus—

100 nitroglycerin require 1·156 naphthalene, or
100 " " 8·03 picric acid

to break up into N, H_2O and CO_2, or

100 nitroglycerin require 14·09 naphthalene, or
100 " " 706·16 picric acid, or
14·16 " " 100· "

to break up into N, H_2O and CO.

As acidity in nitroglycerin is anxiously avoided as a supposed cause of undesired and unforeseen explosions, the admixture of an organic base, such as *aniline*, which is freely soluble in nitroglycerin, may serve the double purpose of neutralising any acid that may be generated by a slow decomposition, and of burning the surplus oxygen which exists in nitroglycerin.

Relinquishing the attempt to obtain total gasification, we return again to explosives which are nearly related to common gunpowder, as their oxidising agents are salts with a non-volatile base.

* Vide H. Sprengel's English patent, No. 2612, Oct. 5th, 1871; and Berthelot, Sur la Force de la Poudre et des Matières Explosives (*Ann. Chim. Phys.* [4], xxiii, p. 265, 1871).

Potassium chlorate is the first that has to be mentioned. *It furnishes detonating explosives when mixed with almost every organic substance.* Such at least was my experience, when I subjected small portions of these mixtures to concussion between iron and iron. As the mixing of potassium-chlorate with combustible substances—at least with solid ones—is a notoriously dangerous operation, *I have, to avoid friction, availed myself of combustible liquids, which, when brought into contact with porous cakes or lumps of potassium-chlorate, are absorbed quietly and without risk.* These lumps or cakes may be formed by pressing into moulds the powdered chlorate, slightly moistened with water. After drying they possess the coherency of lump-sugar, and their porosity depends upon the fineness of the powder and the degree of compression which they have subsequently undergone. These have to be regulated by the volume of the liquid required to be absorbed.

When subjected to the detonation of 0 65 gram of fulminating mercury, these cakes appeared to be non-explosive, unless the liquid absorbed contained a certain amount of sulphur or a nitro-compound. Thus, for instance, they exploded—

Most violently with carbon bisulphide,
,, ,, nitrobenzene,
Violently with $\frac{1}{2}$ benzene + $\frac{1}{2}$ carbon bisulphide,
,, carbon-bisulphide saturated with naphthalene,
Very well with phenol dissolved in carbon-bisulphide,
Well with $\frac{3}{4}$ petroleum + $\frac{1}{4}$ carbon-bisulphide,
Not well with petroleum saturated with sulphur,
,, with benzene saturated with sulphur.

The benzene mixture (without the sulphur) did not explode.

Sulphur seems to be sparingly soluble in hydrocarbons; still there are exceptions, such as naphthalene, which dissolves it more readily. If the decomposition of the carbon-bisulphide mixture should take place as follows:—

$$2(KClO_3) + CS_2 = 2KCl + CO_2 + 2SO_2;$$

100 potassium-chlorate would require 31 carbon-bisulphide. I observed, however, that less carbon-bisulphide (from 15 to 20 parts) gave better results, implying the formation of sulphuric acid.

Such a mixture, used in open granite quarries for blasting, proved to be about four times as effective as the same weight of gunpowder.

Though the benzene mixture (without the sulphur) did not explode under the above conditions, the great similarity which exists between concussion and detonation, suggests that all substances which may be exploded by concussion may likewise be exploded by detonation, sufficiently powerful. *In fact I found, that when I surrounded the percussion cap with an envelope of gun-cotton, its detonating power, thus strengthened*

or multiplied, had the effect of exploding in a most satisfactory manner mixtures of potassium-chlorate, which contained neither sulphur nor a nitro-compound, such as benzene, petroleum, and phenol mixtures. These in the form of cakes weighing 80 grams, exploded with great energy when I subjected them unconfined to the detonation of 15, 8, and 7 grams of gun-cotton.

The practical significance of this fact is obvious.

We owe to Mr. Abel the interesting discovery (*Phil. Trans.*, clix, 1869) that not only the quantity but likewise the quality, *i.e.*, the chemical composition of the detonating agent plays an important part in the propagation of an explosion. Future experiments will show how confinement and the united influence of quantity and quality in the detonator will effect combustible mixtures which have hitherto been considered as non-explosive.

The reaction which takes place between potassium-chlorate and benzene may in its simplest form be represented thus:—

$$\begin{array}{lccccccccc} & \multicolumn{3}{c}{\text{Composition before explosion.}} & & \multicolumn{5}{c}{\text{Supposed composition after explosion.}} \\ & 5KClO_3 & + & C_6H_6 & = & 5KCl & + & 6CO_2 & + & 3H_2O. \\ \text{Equivalent weights} & 613 & + & 78 & = & 373 & + & 264 & + & 54 \end{array}$$

$$\underbrace{88{\cdot}71 + 11{\cdot}29}_{100} = \underbrace{53{\cdot}98}_{\text{solid}} + \underbrace{38{\cdot}21 + 7{\cdot}81}_{46{\cdot}02 \text{ gaseous}}$$

I did not notice any tendency to explosiveness when the above cakes, charged with the combustible liquid, were set on fire.

As in the acid mixtures so here, a great many mutations are possible. Potassium-chlorate may be partly (or perhaps totally) replaced by potassium- or sodium-nitrate. The liquid hydrocarbons mentioned above may be replaced either partly or totally by such which are not volatile. Fat, bitumen, rosin, or a solid hydrocarbon may be used of so low a melting point that it becomes practicable to charge the oxidising cakes with them while in the fused state. As carbon in the form of charcoal, graphite, or diamond shows a different affinity for oxygen, so here the use of a hydrocarbon, or of any other combustible liquid *difficult* to inflame, will lower the tendency which compounds of potassium chlorate have to explode.

At the conclusion of this introductory inquiry some allusion should be made to the aspect of the foregoing subject from a practical point of view. It is true that objections may be raised against the use of some of the foregoing explosives. The acid-mixtures are hygroscopic and inconvenient to handle, on account of the corrosive properties of nitric acid. It is also not easy to find a suitable material out of which to

make the cartridges. We have to choose between glass, stoneware, iron, and (when in the form of dynamite) perhaps paraffin-paper. Still it remains to be seen whether the advantages accruing from their use will not outweigh these disadvantages. In cheapness, power, and safety they compare favourably with other explosives now in use. The oxidising cakes or *grains*, when impregnated with oily liquids, are protected against the action of water. It should be borne in mind that $\frac{9}{10}$ths of all explosives made (including common gunpowder) are used for blasting, and that the valuable properties of common gunpowder as a propelling agent are not required for mining operations. Here we want (with few exceptions) the strongest and the cheapest force. Hence my belief in a future for the above explosives. The great progress which of late years has been made in the manufacture of chlorine promises to lower the price of the chlorates, and nitric acid must always be cheaper than nitro-compounds.

Lastly, though not least, to avoid the danger of a spontaneous explosion of these compounds during their manufacture, storage, and transport, *we can keep apart the oxidising from the combustible agent, until their chemical combination is to take place in obedience to the will of man.* I am aware that this way has been pointed out before, and has been abandoned as impracticable; but formerly both the oxidising and the combustible agents were solids. Now, however, we have two liquids, or a liquid and a solid, rendering their admixture easier.

I feel justified in laying some stress on this point, as it appears to me to be the only path capable of conducting us through the operations necessary for the production and use of these dangerous explosives *in absolute safety.*

XXXIII.—*The Dioxides of Calcium and Strontium.*

By Sir JOHN CONROY, Bart., M.A.

ALTHOUGH the existence of peroxides of calcium and strontium has been known for a considerable time, the fact having been announced by Thénard in 1817, I am not aware of any account of the properties or composition of these substances ever having been published, and therefore beg to lay before the Society an account of some experiments I have lately made.

It is usually stated that lime and strontia, unlike baryta, do not absorb oxygen at a high temperature; but in order to establish the fact that no absorption took place at any temperature, I placed fragments of lime and strontia in the sealed ends of pieces of bent combustion-tube,

which were filled with oxygen and placed over mercury in such a manner that if any absorption took place it could be observed; the ends of the tubes containing the lime and strontia were heated in a sand-bath placed over a large bunsen burner, and subsequently directly by the flame of the burner, till a temperature was reached at which the glass began to fuse; but no absorption took place in either tube, although in a similar tube in which some baryta had been placed, and which was heated in the same sand-bath, the oxygen was readily and completely absorbed at a moderate temperature. These three tubes were placed side by side in the same sand, and dipping into the same trough, and were many times heated and allowed to cool, the temperature being carried a little higher on each occasion.

Sir Benjamin Brodie (*Phil. Trans.*, 1863, p. 409) states that he has ignited lime and strontia with potassium chlorate, but did not succeed in obtaining any higher oxide of either metal, although in the case of baryta this process is an easy method of obtaining a crude peroxide of barium.

As has been mentioned before, the existence of peroxides of calcium and strontium was first announced by Thénard, who obtained the hydrates of these oxides in the form of shining scales, when he added a solution of hydrogen peroxide to lime or strontia water (*Annales de Chimie*, viii, 1817, p. 312).

" Quoiqu'il en soit, lorsque l'on verse un excès d'eau de baryte dans l'acide nitrique ou l'acide hydrochlorique oxigéné, et à plus forte raison sur-oxigéné, il se forme un précipité cristallin d'hydrate de deutoxide de barium. Ce précipité est très-abondant en paillettes nacrées et peu solubles dans l'eau. Celle-ci à 10 degrés le décompose et le transforme en gaz oxigène et en baryte ou protoxide de barium. La strontiane et la chaux sont susceptibles d'être sur-oxidées toutes deux de même que la baryte, par les acides sur-oxigénés. L'hydrate de deutoxide de strontium ressemble beaucoup à celui de barium; celui de chaux est en paillettes plus fines."

In order to repeat his experiments I caused some sodium peroxide to be prepared by heating metallic sodium in a flask through which air carefully freed from carbon dioxide and moisture, and then pure and dry oxygen were passed, until the sodium was completely converted into peroxide. (Compare Mr. A. Vernon Harcourt's paper, *Chem. Soc. J.*, xv, 267.)

This substance affords a ready means of preparing these dioxides, as on the addition of an aqueous solution of sodium peroxide to the solution of a salt of strontium, the hydrated dioxide of that metal forms in shining scales having a pearly lustre. With calcium the case is somewhat different, as when a neutral or alkaline solution of sodium peroxide is added to the solution of calcium salt, the hydrated dioxide

of this metal is thrown down in the form of an extremely finely divided white precipitate. It appears almost impossible to obtain the substance pure in this form, as, in addition to its being exceedingly difficult to filter from its finely divided condition, it decomposes very readily. When, however, a considerable excess of lime water is added to a solution of sodium peroxide rendered acid by hydrogen nitrate, the dioxide forms slowly in scales somewhat similar in appearance to the corresponding strontium compound.

Calcium Dioxide.

The calcium peroxide obtained in this manner was well washed and dried on blotting-paper, a sheet of gutta-percha being folded round the paper to preserve the peroxide from the air.

Sir Benjamin Brodie has shown that hydrogen peroxide and potassium permanganate decompose each other, an equal amount of oxygen being given up by either substance. This reaction afforded an easy means of estimating the amount of oxygen contained in the peroxide of calcium and strontium when dissolved in a dilute acid.

Three preparations of calcium peroxide obtained in the beforementioned manner gave the following results on analysis:—

No. 1. ·0993 gram of the peroxide gave ·0625 gram of calcium sulphate.

·1257 gram of the peroxide gave ·0784 gram of calcium sulphate.

·0674 gram of the peroxide reduced 12·65 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.

·0859 gram of the peroxide reduced 16·45 c c. of the same permanganate solution.

No. 2. ·1123 gram of the peroxide gave ·0688 gram of calcium sulphate.

·1053 gram of the peroxide gave ·0616 gram of calcium sulphate.

·1214 gram of the peroxide reduced 23·95 c.c. of the same permanganate solution.

·0891 gram of the peroxide reduced 17·2 c.c. of the same permanganate solution.

·0545 gram of the peroxide reduced 10·7 c.c. of the same permanganate solution.

No. 3. ·1340 gram of the peroxide gave ·0858 gram of calcium sulphate.

·0637 gram of the peroxide reduced 12·7 c.c. of the same permanganate solution.

When the hydrated calcium peroxide is heated in a current of dry carbon dioxide, the whole of the water is driven off, together with half the oxygen contained in the substance, and calcium carbonate is formed.

·4588 gram of the peroxide was placed in a weighed silver boat and heated in a combustion-tube by a small bunsen burner, whilst a current of dry carbon dioxide was passed over the substance, and the water collected in a weighed calcium chloride tube; ·2106 gram of carbonate and ·3017 gram of water were obtained. These numbers agree best with a substance, having for its composition $CaO_2.8H_2O$.

	Theoretical.		Prep. 1.		Prep. 2.			Prep. 3.	
CaO ..	56	25·92	25·91	25 68	25·22	25·28		26·36	25·70
O	16	7·40	6·79	6·93	7·14	6·99	7·11	7·22	—
$8H_2O$..	144	66·66	—	—	—	—		—	65·76

The hydrated calcium peroxide decomposes slowly when it is allowed to remain in the solution from which it has been precipitated, but when dry, provided it is kept from the air, or rather from the carbon dioxide contained in it, it is a stable substance.

When the hydrate of calcium peroxide is heated to about 100° in a current of dry air free from carbon dioxide, the substance loses its crystalline appearance, the water it contains is driven off, and anhydrous calcium peroxide is left in the form of an extremely light and very pale buff-coloured powder. It is scarcely, if at all, soluble in water, but dissolves readily, without any evolution of oxygen in dilute acids, even in hydrogen acetate. It is also soluble in ammonium chloride, but not in ammonium hydrate.

(1.) ·1869 gram of the hydrate was heated in a weighed silver boat which was placed in a piece of combustion-tube heated in a water-bath, and air carefully dried and free from carbon dioxide was passed over it for half an hour, the temperature of the bath being 100°; the hydrate lost ·1213 gram, and ·0639 gram of the resultant substance reduced 32·75 c.c of a solution of permanganate, of which 1 c.c. contained ·0003622 gram of oxygen.

(2.) ·0940 gram of the hydrate heated to 100° for an hour lost ·0612 gram, and ·0313 gram of the residue reduced 16·2 c.c. of the permanganate solution.

(3.) ·0914 gram of the hydrate heated to 100° for an hour, lost ·0590 gram, and ·0306 gram of the residue reduced 15·4 c.c. of permanganate.

(4.) ·1116 gram of the hydrate heated to 128° for an hour, lost ·0722 gram, and ·0380 gram of the residue reduced 19·8 c.c. of permanganate.

These numbers give the percentage loss of weight in the four cases

as (1), 64·90; (2), 65·10; (3), 64·55; (4), 64·69, and the amount of oxygen in the residue as (1), 18·57; (2), 18·74; (3), 18·23; and (4), 18·87.

The theoretical loss of weight is 66·66 per cent. and 22·22 per cent. of oxygen ought to have been found in the residue, supposing it to have consisted of pure anhydrous calcium dioxide. The difference in all probability was caused by the original hydrated calcium dioxide having contained some calcium hydrate, which would still retain its water at a temperature sufficiently high for the dehydration of the dioxide.

Strontium Dioxide.

As has been before mentioned, when the solution of a salt of strontium is added to an aqueous solution of sodium peroxide, the hydrated peroxide of strontium forms in crystalline scales.

At the ordinary temperature, this substance begins to decompose almost as soon as it has formed, but when the solutions are cooled down to about 5°, it no longer decomposes so readily.

After this dioxide has been washed and dried on blotting-paper, it is a stable substance very similar in appearance and behaviour to the corresponding calcium compound. A specimen of this substance gave on analysis the following results:—

·5460 gram heated whilst carbon dioxide was passed over it, gave ·2940 gram of water, and ·3096 gram of strontium carbonate.
·1672 gram yielded ·1154 gram of strontium sulphate.
·1706 „ „ ·1192 „ „ „
·1562 gram reduced 25·05 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.
·2042 gram reduced 32·3 c.c. of the same permanganate solution.

These numbers correspond best with the theoretical composition of a hydrate containing 8 molecules of water.

	Theoretical.				
SrO......	103·5	39·28	39·79	38·93	39·41
O........	16·0	6·07	5·80	5·73	—
$8H_2O$	144·0	54·65	53·846	—	—

Under slightly different conditions, strontium dioxide appears to form two other fairly stable compounds with water—in one twelve molecules, and in the other ten molecules of water are present.

The analysis of the 12-molecule substance gave the following results:—

·3206 gram of the substance reduced 38·35 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·00036025 gram of oxygen.

·0639 gram reduced 8·25 c.c. of the same solution.
·6671 gram yielded ·3671 gram of strontium sulphate.

·4968	„	„	·2769	„	„	„
·8807	„	„	·3870	„	„	carbonate, and
			·5696	„	water.	

These numbers give the percentage composition as—

	Theoretical.						
SrO......	103·5	30·85	—	—	31·03	31·43	30·83
O........	16·0	4·77	4·59	4·65	—	—	—
$12H_2O$....	216·0	64·38	—	—	—	—	64·67

The analysis of the 10-molecule substance gave the following results :—

·1325 gram of the substance gave ·0819 gram of strontium sulphate.

·1384 gram of the substance reduced 19·95 c.c. of a potassium permanganate solution, which contained ·0003622 gram of oxygen in 1 c.c.

·1852 gram of the substance reduced 26·35 c.c. of the same permanganate solution.

·7164 gram of the substance gave ·3539 gram of strontium carbonate.

·7056 gram of the substance gave ·3444 gram of strontium carbonate and ·4188 gram of water.

The percentage composition of the hydrate of strontium dioxide, as deduced from these figures is as follows :—

	Theoretical.					
SrO	103·5	34·55	34·86	—	34·66	34·25
O	16·0	5·34	5·221	5·153	—	—
$10H_2O$	180·0	60·10	—	—	—	59·35

When these different hydrates of strontium dioxide are heated to 100° in a current of dry air free from carbon dioxide, they lose all the combined water, and the anhydrous dioxide is left in the form of a white powder. It is little if at all soluble in water, but alters slightly in appearance when mixed with it.

It is entirely soluble in dilute acids, even in hydrogen acetate, without any evolution of oxygen; and also in ammonium chloride, but not in ammonium hydrate.

·2189 gram of the hydrate containing 8 molecules of water lost in 30 minutes at 100°, ·1180 gram, and ·0997 gram of the residue reduced 34 c.c. of a solution of potassium permanganate, of which 1 c.c. = ·0003622 gram of oxygen.

·1410 gram of the same hydrate lost under similar circumstances ·0753 gram, and ·0651 gram of the residue reduced 21·85 c.c. of the same permanganate solution.

The percentage loss of weight in the two cases is 53·9, and 53·4, and the amount of oxygen in the residue 12·35 and 12·16 per cent. Theoretically, the loss of weight should have been 54·65, and 13·39 per cent. of oxygen ought to have been found.

·2633 gram of the hydrate containing 10 molecules of water lost ·1568 gram at 100° in 60 minutes, and ·1034 gram of the residue reduced 39·95 c.c. of the same permanganate solution.

·1364 gram. of the same hydrate lost ·0816 gram at 100° in 40 minutes, and ·0540 gram of the residue reduced 18·9 c.c. of the same permanganate solution.

The percentage loss of weight, as deduced from these numbers, is 59·55 and 59·82, and the amount of oxygen found 12·59 and 12·68. Theoretically, the loss of weight should have been 60·1.

·3934 gram of the substance containing 12 molecules of water lost ·2454 gram on being heated to 100° for 30 minutes, and ·1461 gram of the residue reduced 48·4 c.c. the same permanganate solution.

·2128 gram of the same hydrate lost under similar conditions ·1328 gram, and ·0794 gram of the residue reduced 26·15 c.c. of the same permanganate solution.

The loss of weight was 62·38 and 62·41 per cent., and 12 0 and 11·93 was the percentage of oxygen in the residue. Theoretically, the substance should have lost 64·38 per cent.

I have not as yet been able to devote any time to the investigation of the conditions under which these different hydrates of strontium dioxide are formed; and as just at present I have not sufficient leisure to go on with the enquiry, I think it best to lay before the Society some account of the experiments I have already made; and I hope at no distant date to have the honour of bringing under the notice of the Society some further account of these substances, and of their properties.

In conclusion, I must add that my best thanks are due to Mr. Harcourt, not only for the use of the Christ Church laboratory, where these experiments were made, but also for the many valuable suggestions and the assistance he has given me during their progress.

XXXIV.—*On Iodine Monochloride.*

By J. B. Hannay.

The chlorides of iodine, although substances of great interest as regards chemical theory, and curious as regards their own properties, have as yet been studied by chemists to very little effect; indeed textbooks give entirely different descriptions of their properties and constitution. The monochloride, standing as it does in the same position as bromine, seemed to offer an interesting and productive field for work. Concerning the properties of this body, chemists express diverse opinions, some describing it as a liquid, and others as a solid, some saying that it dissolves in water without decomposition, while others again say that water instantly decomposes it. Most of those chemists who have examined this body, seem to have done only a little work and then abandoned it; but P. Schützenberger—whose memoir in 1862 is the only one I can find which gives anything like a definite account of the preparation and properties of this substance—seems to have followed at least a definite plan of work.

The monochloride of iodine may be prepared in two ways: the first is to pass chlorine gas into iodine until it is liquefied, and rectify the product so obtained between 100° and 102°. I have found that this liquid has a little of the trichloride always mixed with it, from which, however, it may be freed by distilling once or twice off iodine at 100° to 102°. If it be not distilled off iodine, it is extremely difficult to free it from the trichloride, and it will be found that on distilling, when the temperature reaches 90° or 95°, a yellow sublimate of the trichloride will be invariably formed. The second method of preparing the monochloride is to mix iodine and potassium chlorate, and heat in a retort, when the liquid distils over almost pure. To purify it completely, simple distillation off potassium chlorate is sufficient, when it will be found that the whole liquid distils between 100° and 102°. The liquid thus obtained will sometimes remain liquid for five or six days after distillation, but generally before that time it will have crystallised. I tried a few experiments by heating iodine with metallic chlorides, but none of those tried gave any of the chlorides of iodine; the only interesting result being that when arsenic trichloride and iodine are heated together, the iodine dissolves in the trichloride without chemical action, giving the liquid a deep reddish-purple colour, and crystallising out on cooling in plates. If the two substances are distilled together, the iodine volatilises in violet vapours together with the arsenic trichloride.

The most curious property of iodous chloride is, that when recently distilled it sometimes remains liquid even when cooled down to $-6°$, but will always bear a temperature of 2° or 3° without solidifying, although its melting point is 24·7°; but after it has been kept for several days, it at once solidifies when the temperature is allowed to fall a few degrees below its melting point. When the compound has been allowed to solidify, and then melted by the application of a gentle heat, it crystallises at once when the temperature reaches 24°, but on distilling the same liquid it may be easily cooled to 2° or 3° without crystallising. If, however, the liquid, even when recently distilled, be cooled to 24°, and then brought into contact with a crystal of its own kind, crystallisation immediately sets in, and in a short time the whole mass is solid. The following experiment curiously illustrates this sudden crystallisation. If two tubes be taken, one containing the compound in the liquid, and the other in the solid state, and the contents of the former slowly poured into the tube with the solid, crystallisation sets in so energetically that crystals are seen to shoot up the running stream until they reach the liquid in the second tube, when in a moment the whole becomes solid. Another curious phenomenon which I observed was the following:—A portion of the liquid which had been standing for two days, was raised in temperature to 24° and a thermometer introduced. A crystal of the solid was then dropped in, and, when the whole had quickly assumed the crystalline form, the thermometer was observed to rise to 27°, although the melting point of the chloride is fully 2 degrees lower. The solid (almost indeed before it was completely formed) began to melt, and in about a minute nearly half of the crystals had become liquid. It would thus seem, that the liquid after standing is so prone to pass into the solid form, that when a crystal is presented to it, the molecules arrange themselves so quickly in a geometrical form, that the heat evolved has not time to act till after the solid condition has been assumed. Another curious instance of the crystallisation of this compound is the following:—A stoppered bottle containing the liquid recently distilled, was laid aside in a still place, when, after three days the substance was still liquid, but round the stopper in the upper end a cluster of shining crystals of the solid compound had grown. I continued to watch them, and day by day they grew longer and larger, till they reached half way down the side of the bottle. One day while examining them, I happened to shake the bottle, and whenever the liquid touched the lowest crystal, the whole became solid. It would thus appear that the liquid compound, as first distilled, has a different molecular arrangement from the solid, and that the molecules of the liquid, when allowed to stand, slowly re-arrange themselves, and then crystallisation sets in. It may be the same with the gas, the liquid slowly giving off the vapour, which, after re-arrange-

ment of its molecules, is deposited on the rough ground part near the stopper in the crystalline form. The crystallisation of iodine chloride in its energetic character resembles very much that of vanadium pentoxide. Both substances, when passing from the liquid to the solid state, do not, like ice, form a solid mass, but the crystals separate out, and sometimes even start up above the level of the liquid, leaving empty spaces between them; so that, if a thin layer of the liquid be allowed to cool, it will, on crystallising, arrange itself in definite crystals, leaving the vessel containing it quite bare between them. The colour of both iodine monochloride and vanadium pentoxide when liquid is deep red, and, when crystallised, of a brilliant plumbago or iodine lustre. As far as I have noticed, however, vanadium pentoxide cannot, like the iodine-compound, be cooled much below its melting point without crystallising. The usual crystalline form of iodine monochloride is in thin flat plates. If the inside of a bottle be wet with the liquid and allowed to cool, the liquid on crystallising runs into the most beautiful fern- or fan-like figures. When good crystals are obtained by the direct condensation of the vapour into the crystalline form, they generally differ from those obtained from the freezing of the liquid, in being thick. They are seen to be of cubical form, generally arranged in a straight line so as to form a quadrangular needle, but sometimes they grow slanting, that is, one crystal growing a little to the side of the other so as to form a line divergent from the vertical.

To determine the melting point of this compound, it was necessary to obtain a pure product, which was effected as follows:—A portion of the liquid was distilled, and the part boiling from 100 5° to 101·5° was collected separately; this was cooled down, and a crystal of its own kind brought in contact with it, when crystallisation set in. The flask containing the crystals was inverted to let them drain quite free from any liquid with which they might be associated. A small quantity of the solid was then taken out and placed in a tube having a capillary point This was fixed to a thermometer and placed in water, then gently heated. At 24·5° the crystals were seen to adhere to the glass but did not melt, but at 24·8° they began to melt, and after standing at that temperature a short time longer, they entirely became liquid. The following numbers are obtained from eight experiments conducted as above:—

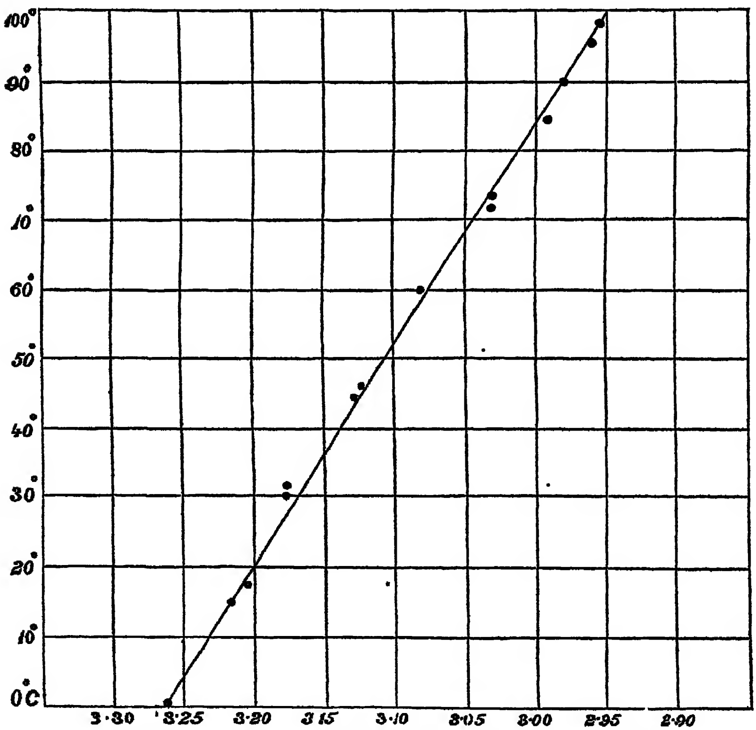
$$24{\cdot}8+24{\cdot}9+24{\cdot}7+24{\cdot}4+24{\cdot}6+24{\cdot}7+25{\cdot}0+24{\cdot}5=197{\cdot}6\div 8=24{\cdot}7.$$

We thus see that the average melting-point of the pure compound is 24·7°. The density of iodine monochloride at 16·5° is 3·222. I wished to ascertain what variation in density a rise of temperature would occasion, so I determined the density at various temperatures ranging from 0° to 100°. For temperatures below 24° recently distilled

liquid had to be used. The following numbers give the densities obtained at vaiious temperatures:—

Temperature.	Specific gravity.	Temperature.	Specific gravity.
0°	3·263	60°	3·084
16·5°	3·222	72°	3·032
18·2°	3·206	75°	3·036
30·0°	3·180	86°	2 988
32·0°	3·176	90°	2·984
45·0°	3·132	95°	2·964
48·0°	3·127	98°	2·958

If these numbers be graphically represented, as in the following diagram, they approximately form a straight line, showing that iodine chloride expands equally for each equal increment of temperature, even near its boiling point. This is rather curious, especially in a compound whose constituents are so loosely held as in this chloride:—



It was necessary, when preparing a substance so little known as

iodine chloride, to determine carefully its vapour-density, and thus arrive at a conclusion as to the purity and stability of the compound. The first determination gave 79·3 as its vapour-density, the calculated number being 81·2. In this experiment the bulb was sealed at 123°. This was pretty near the required number, but, to leave no doubt, another was taken with a more carefully-prepared and purified compound. This was sealed at 120°, and gave 80·29 as the vapour-density.

I wished to find if a high temperature would have any effect on the vapour-density of the chloride, so I determined it in the following manner:—Two tubes of thin hard glass were drawn out in the manner of those used for estimating nitrogen as ammonia, and placed side by side resting on wire-gauze, in a concave iron tray. Another iron tray (in which were two holes), fitting closely to the lower tray, served as a cover. The small tubes from the two tubes in the iron tray were allowed to project from the holes. The tubes were carefully weighed, and iodine chloride placed in one, while into the other was put some iodine. The cover was placed on them and the under tray heated red hot. The two tubes were now under precisely the same conditions, lying side by side close together. When the temperature was judged to be high enough, the tubes were sealed and the contents of each determined as in an ordinary vapour-density. The iodine tube was of course to serve merely as a thermometer. The temperature was first approximately calculated; then the corrections made in both cases for expansion of the glass; and finally the temperature was calculated by the following formula, the measurements having been made at 15°.

$$X = \frac{127 \times \cdot 0896 \times 273 \times 288\,C}{288W \times V(127 \times \cdot 0896 \times 273)} - 273$$

C = capacity of bulb in litres. W = weight of iodine vapour.
V = volume of residual air in litres. X temperature required.

The temperature of the bulb was, in the experiment which I made, 512°; at this temperature the vapour-density found was 83·2. This is a little too high, but, considering the difficulties, it is near enough to show that no material change occurs on heating.

To determine the relative amounts of chlorine and iodine in the compound, the following method was employed:—A portion of the liquid was decomposed by water, and then as nearly as possible neutralised with potassium hydrate. The solution was evaporated to dryness, and the salt heated to expel oxygen, and reduce the salts to the state of chloride and iodide. This was then dissolved in water and nitrate of silver added, then nitric acid, to dissolve any oxide of silver which was precipitated by the slight excess of potassium hydrate which was almost invariably present. The mixed chloride and iodide of

silver were weighed together, and then reduced to the metallic state by fusion with potassium cyanide. The silver is thus obtained in a coherent light-coloured mass, which shows the bright metallic lustre of silver when pressed with a stirring-rod. After boiling this repeatedly with water to remove potassium salts, the silver is obtained quite pure, and may be heated red-hot in a crucible and weighed, or it may be fused on charcoal and weighed as a bead. By a simple calculation from these two weighings, it is easy to find the relative amounts of chlorine and iodine. Let us take, for instance, the following analysis. The mixed silver salt was found to weigh 1·9000 gram; on reduction this weighed 1·0850 gram To find the relative amounts of chlorine and iodine, the silver was calculated to chloride; this gave 1·4415 gram. On subtracting this from the total salts, a number was obtained which denotes the increase caused by the presence of iodide, which was found to be 0·4585 gram. Now if this number be multiplied by 127, the combining weight of iodine, and divided by 91·5, the difference between chlorine and iodine, the amount of iodine in the original compound is obtained, which was found, in this case, to be 0·6363 gram. Again, if the amount of the metallic silver found be subtracted from the amount of the double salt, we get the amount of chlorine and iodine in this case 0·8150; and by subtracting the amount of iodine above obtained from this, the remainder of course gives the chlorine, which was found to be in this case 0·1787. If we now divide each of these numbers by the combining weight of the respective elements, we obtain the number ·0050 in each case, showing that the relative amounts of chlorine and iodine agree with the formula ICl.

When iodine chloride is decomposed by water, iodine is precipitated and a deep red solution formed; and on adding carbon disulphide to this after filtering off the iodine, a red solution is obtained, which resembles a solution of the ordinary monochloride, and reacts exactly as a solution of this substance in carbon disulphide. On adding iodine monochloride to water, the following reaction takes place—

$$5ICl + 3H_2O = HIO_3 + 5HCl + 2I_2;$$

the hydrochloric acid formed dissolves a portion of the still undecomposed iodous chloride, and thus gives the solution a red colour. At first I thought it might be the iodine which was dissolved, giving the solution the red colour, but as stated above, on agitating with carbon disulphide, a red colour is obtained, clearly showing that it cannot be iodine. On adding solution of potassium hydrate drop by drop, to neutralise the hydrochloric acid found, the whole of the compound is decomposed, and the iodine precipitated, the reaction being as follows:—

$$5ICl + 6KHO = KIO_3 + 5KCl + 2I_2 + 3H_2O.$$

That the red colour is due to a solution of iodine chloride in the hydrochloric acid is also shown by the following experiment. On adding iodine chloride to hydrochloric acid of boiling point 110°, a fine red-coloured solution is obtained without any separation of iodine, and on agitating this with carbon disulphide, the same red solution is obtained as with the ordinary chloride. On heating, it is curious to observe that the boiling point of the hydrochloric acid is unaltered, and that no iodine chloride distils over at 102°, but it all comes over at 110° with the hydrochloric acid. It does not matter whether only a drop or two of the iodine chloride has been added to the hydrochloric acid, or as much as a third; the boiling-point is the same, viz., 110°. If the red solution of iodine chloride in hydrochloric acid be treated with water and carbon disulphide, and allowed to stand about a fortnight, the iodine chloride is completely decomposed, the iodine being in solution in the carbon disulphide, while the water contains nothing but iodic and hydrochloric acids. When the chloride is decomposed by water, it will also be noticed that the amount of iodine precipitated increases with the time it is left after precipitation, and on filtering off the iodine at once from a portion decomposed by water, it will be found that a precipitate soon gathers in the filtered liquid, and on filtering off this, the same happens again and again, the amount lessening each time; but in no case is the whole compound decomposed, even after several days, a large proportion remaining in solution. I have tried various experiments with chlorinating agents, and have failed to prepare the substance described by Kämmerer as iodine tetrachloride. I have also had iodine chloride under all conditions for lengthened periods, but I have never noticed the spontaneous decomposition of the monochloride into the tetrachloride and free iodine which he says took place. I doubt the existence of this compound. I have, however, often noticed the splitting up of the monochloride into trichloride and iodine, mentioned by Kane, this reaction taking place nearly every time the monochloride is distilled.

I have examined the action of iodine monochloride on several elements and compounds, and as some are very interesting, I shall give them in detail.

With tin in foil it unites with a hissing sound, and evolution of white fumes of stannic chloride and violet vapours of iodine.

With antimony in powder it unites, with great evolution of heat and hissing sound, while violet vapours of iodine are evolved. The products are chloride and iodide of antimony.

Arsenic in powder unites with this chloride with violence, burning with a pale flame and hissing sound, while white vapours of arsenic trichloride and a little iodine are evolved. The residue is liquid at first, but crystallises on cooling. It is entirely soluble in water, and yields

iodide of arsenic on evaporation. Bismuth unites with less vehemence than antimony, the products being chloride and iodide of bismuth.

Mercury combines quietly with iodine chloride to form mercuric chloride and iodide.

Galena in powder unites with the chloride, with evolution of fumes, to form chloride of sulphur and iodide of lead.

Copper unites when in the finely-divided state, with iodine chloride, with evolution of heat and a hissing noise, iodine fumes being meanwhile evolved; the products are principally cuprous chloride and iodide, but a little cupric chloride is generally formed. On copper-foil its action is very slow, and it takes weeks before even a small quantity of iodine chloride completely combines with the copper. The surface of copper remains bright for a few minutes when immersed in liquid iodine chloride.

If aluminium foil be wetted with iodine chloride, and allowed to stand, no action seems to take place at first, but after a short time a hissing sound is heard, and suddenly the aluminium burns with a bluish white light, sometimes very bright, and sending out bright sparks. Sometimes it suddenly glows all over, and with a hissing sound combines with the chloride.

Magnesium in filings unites directly with the chloride almost without evolution of heat, to form iodide and chloride of magnesium.

The difference in the deportment of potassium and sodium when introduced into the liquid is very curious. The potassium at once explodes, and when a piece of half the size of a pea is placed in the liquid, the explosion is sometimes very loud, even breaking the vessel which contains it. Sodium, on the other hand, when introduced, does not show any action whatever, not even by a rise of temperature, except where several small pieces are simultaneously introduced, when a slight rise of temperature is the result. When sodium is rubbed in a mortar with iodine chloride, a quiet union of the elements to form iodide and chloride of sodium is the result, without much heat being evolved.

With sulphur the action is very faint. When flowers of sulphur are sprinkled into the liquid, they are absorbed without almost any rise of temperature, while a small quantity of white fumes are evolved. Iodide and chloride of sulphur are the result.

Selenium unites with iodine chloride with a hissing sound, while dense fumes of selenium chloride are evolved.

Tellurium acts still more energetically than selenium, hissing fiercely when dropped into the chloride.

Ordinary phosphorus bursts into flame when treated with iodine chloride, but amorphous phosphorus only hisses, and emits fumes mixed

with iodine vapour. The liquid has no action upon either crystalline or amorphous silicon.

Bromine mixes with iodine chloride in all proportions, without seeming to have any action. Iodine chloride dissolves in carbon tetrachloride without action, forming a red solution. When iodine chloride is added to carbon disulphide till saturated, small quantities of white fumes, which smell like sulphur chloride, are evolved, and on treating the product with water, sulphur is precipitated, and a heavy oily body sinks to the bottom. This was found to be a mixture of carbon disulphide, tetrachloride, and sulphochloride. This action of iodine chloride on carbon disulphide is still more decided on distilling the mixture, when the distillate fumes distinctly, and the smell of the sulphochloride is very decided while iodine remains in the retort.

On distilling the chloride of iodine from potassium iodide several times, it is entirely converted into iodine, while potassium chloride is formed, $KI + ICl = KCl + I_2$. The distillation requires to be repeated several times before the conversion is complete.

The action of iodine chloride on the skin is more energetic than that of bromine or iodine. When a spot gets on the face, even when the liquid is at once washed off with water, it quickly eats through the skin with a very sharp burning pain, and even causes sores difficult to heal. It causes a permanent stain, and even months after the sore is healed, the place is plainly marked by a reddish-brown spot.

XXXV.—*On Sulphur Bromide.*

By J. B. Hannay.

The uncertainty which overhangs the composition of sulphur chlorides induced me to work upon the less known sulphur bromide, thinking that as bromine is nearer the solid state than chlorine, I might be able to obtain more stable and definite compounds.

This, however, I find is not the case. The lower chloride of sulphur can at least be distilled, and has moreover a definite boiling-point, whereas the bromine-compound formed by the union of the elements in atomic proportions cannot be distilled without decomposition. On adding sulphur to bromine in the proportion of 32 to 80 to form SBr, a little heat is evolved, and a deep red liquid formed which fumes but slightly and has a specific gravity of 2·629. When this liquid is submitted to distillation, it begins to boil a little above the boiling-point of

bromine, and the thermometer steadily rises without one continued pause till only sulphur remains. The products obtained by distillation contain an increasing quantity of sulphur as the thermometer rises, so that no definite product can be obtained in this way. The product with which the following experiments were tried was obtained by adding the two elements in atomic proportions and filtering the liquid so obtained through asbestos. In this way a deep red liquid was obtained which, in some cases, acts as if it were only a solution of sulphur in bromine, but in others it seems to be a chemical compound, though of a very weak nature.

The first circumstance which threw doubt on its being a chemical compound was the following. A thin layer of the liquid had been standing in a conical flask exposed to the air, so that the moisture might act upon it slowly. After the action had gone on for a week or so, it was seen that the sulphur which separated was beautifully crystallised and easily and completely soluble in carbon disulphide. Now if the sulphur in this liquid were in actual chemical combination with the bromine, it should play an electro-negative part and the sulphur deposited by the action of water should, according to Berthelot, be insoluble in carbon disulphide. Moreover, the crystals obtained as above are octohedral and very perfect, but some are curiously modified. The description of these crystals is given at the end of this paper.

I thought that the crystalline form and solubility of the deposited sulphur might be due to a slow molecular change, as is noticed in my paper on Iodine Monochloride, so I settled this point by examining quickly deposited sulphur in the following manner:—

Some of the sulphur bromide was shaken up with water, when a part was decomposed, with formation of a white milky liquid above the excess of bromide. Some of this milky liquid was poured into a tube and carbon disulphide added, and after about five minutes' agitation nearly the whole of the sulphur which had been in suspension was dissolved in the disulphide, while the water had lost its milky colour. On evaporating the disulphide of carbon, sulphur was left, showing that the sulphur, contrary to what would be the case if it played an electro-negative part, was quite soluble in carbon disulphide. These are the experiments which at first led me to suppose that this liquid was merely a solution of sulphur in bromine, but the following experiment reassured me of its being a case of real chemical combination, although of a weak nature.

I found that bromide of sulphur dissolves phosphorus with evolution of heat. Thinking that there might be formed a sulphobromide of the formula $PSBr$, I saturated the bromide with phosphorus and heated it slightly till it would take up no more. I allowed the liquid to cool

and settle, and then decanted it from the undissolved phosphorus into a distillation-bulb fitted with a thermometer and proceeded to heat it very cautiously. The liquid was just beginning to boil when it seemed to take fire inside, and vivid combustion ensued for about a second, when the whole exploded with a brilliant flash and loud noise, shattering the apparatus and hurling the ignited combustible all about the room.

The only reason that can be assigned for the phosphorus not exploding when dropped into the bromide is that the elements were in chemical combination and only acted as a solvent for the phosphorus till heat was applied. This is a nice illustration of the difference between solution and chemical combination, and shows that although the phosphorus is, so to speak, eager to combine with both elements in whose compound it is dissolved, it cannot do so until the atoms of the molecules are caused to vibrate strongly, and thus overcome the attraction of chemical combination.

Bromide of sulphur has no apparent action on amorphous phosphorus. Potassium and sodium when dropped into bromide of sulphur, if in pieces of the size of half a pea, do not take fire, but quietly combine with the sulphur and bromine. If, on the other hand, they are very small or thin, they take fire, or at least hiss and become incandescent.

Aluminium in foil remains quite bright when immersed in sulphur bromide; antimony in powder combines with the bromide with a hissing sound, but does not become incandescent.

Arsenic combines, with evolution of heat, to form a colourless liquid of peculiar disagreeable odour, which emits scarcely any fumes. The same liquid can be formed by the action of sulphur upon arsenic bromide. This substance is being investigated.

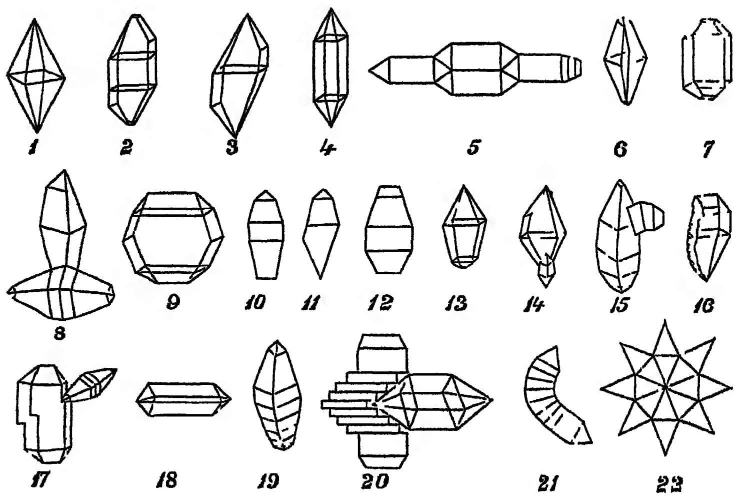
On mixing the bromide with methylated spirit, heat is evolved and sulphur is precipitated, while a sharp sour-smelling liquid is formed which irritates the membrane of the nose.

Bromide of sulphur mixes with iodine monochloride, and double decomposition then takes place, sulphur chloride and iodine bromide being formed.

The crystals of sulphur before mentioned were so perfect, and in some cases so curious, that I thought it might not be out of place to sketch out a few of the most curious. The crystals had generally a greenish tinge intermixed with the yellowish-red. I could not find one crystal belonging to the prismatic form of sulphur in the whole of those crystals which came under my notice.

The crystals were generally large enough to sketch easily without the aid of a lens, but some were microscopically small, as Nos. 5, 20, and 22, which were drawn with the camera lucida. No. 20 is very curi-

ously modified; the centre of one crystal seems to have grown to the point of another in graduated steps. No. 22 consists of eight of the octohedral crystals forming a star. Nos. 13, 14, and 16 were the only crystals which were yellow and beautifully transparent, like some specimens of native sulphur. In No. 17 the small crystal growing to the side of the principal seems to have caused a displacement. No. 21 is a curious case of a bent crystal, and this specimen was very complete. Nos. 9 and 18 seem to belong to the same class, but No. 18 consists of the two ends of the crystal, while No. 9 has a body. Sometimes we get curious mixtures of crystals, as in No. 13, where we have the regular crystal at the top and a modification at the bottom, or in No. 8, where one side of the crystal is regular and the other modified.



XXXVI.—*On Triferrous Phosphide.*

By R. Schenk.

Some time ago Mr. Oppenheim attempted to prepare metallic phosphides by the action of phosphorus on metallic solutions, which were kept alkaline in order to prevent the formation of any salts of the metal with acids of phosphorus. He used ammoniacal solutions of copper, nickel, silver, and zinc, and solutions of lead, cadmium, and tin

in potash. He succeeded in obtaining a phosphide of nickel, but mixed with a salt of some acid of phosphorus. In the case of cadmium, a mixture of the phosphide with some other substance was obtained, the mixture yielding pure phosphide of cadmium on being heated in a current of hydrogen. The other metals gave negative results.

Not knowing anything of Mr. Oppenheim's researches, I was also led to make experiments on the action of phosphorus on alkaline metallic solutions; but as I expected results, not from the direct action of the phosphorus, but from that of the phosphoretted hydrogen, I used only solutions of the metals in potash, and boiled them with phosphorus.

I first tried the action of phosphoretted hydrogen on an alkaline solution of copper. As I did not at once obtain favourable results, owing to the difficulty of preventing the reduction to metallic copper, I began to make experiments on iron, in which case the reduction to the metallic state was not to be feared, and as I had noticed that the *suboxide* of copper, which in alkaline copper solutions is formed by the action of the phosphorus, is speedily converted into phosphide of copper, I did not use an alkaline solution of iron, but poured a solution of ferrous sulphate into a flask in which phosphoretted hydrogen was evolved by the action of potash upon phosphorus. The precipitate of ferrous hydrate formed rapidly turns grey, and then after about 10 or 15 minutes, black. A white froth forming over this liquid, shows that a large quantity of gas continues to be given off, but this gas seems to be chiefly hydrogen.

I went on boiling for about an hour; then removed the greater part of the phosphorus which was left undissolved; added more potash; and boiled again for about half an hour in order to dissolve all the phosphorus. After this I allowed the black precipitate to settle down; poured the greater part of the liquid off; added hydrochloric acid; and boiled for a short time in order to dissolve any oxides and any salts of iron with phosphorus-acids that might have been formed. As some magnetic oxide of iron was present, which is formed by prolonged boiling of ferrous and ferric oxide with potash, I used strong hydrochloric acid. Then I added water and washed the black powder which had remained undissolved, first by decantation, and at last on the filter with water, alcohol and ether. As I had noticed that the copper phosphide when moist oxidised most rapidly in the air, I performed the filtering in a current of carbonic acid.

The substance was now brought into a test-tube immersed in boiling water, and as much as possible dried in a current of carbonic acid.

As the black substance thus obtained still yielded a small quantity of iron to cold dilute hydrochloric acid, I took a small quantity, about

1 gram, and purified it for analysis by again boiling it with hydrochloric acid, and washing it by decantation only, with water, alcohol, ether, and bisulphide of carbon.

The last liquids were not used to get rid of any phosphorus, as this had been removed completely by potash, but only for the purpose of drying as quickly as possible.

The substance was freed from bisulphide of carbon by heating it to 100° in a current of carbonic acid, and then it was transferred in a glass tube, and also in a current of carbonic acid, heated gently over the flame. It was then found to lose about 1 per cent. in weight.

It was then analysed and gave the following results: 0·2215 gram gave ·227 Fe_2O_3 and 0·226 $Mg_2P_2O_7$; ·113 gram gave ·1165 Fe_2O_3 and 0·1145 $Mg_2P_2O_7$. These numbers agree with the formula Fe_3P_2.

	Calculated.	Found.	
Fe......	72·17	71·74	72·11
P	27·89	28·48	28·3.

This compound is the only phosphide of iron in which phosphorus appears trivalent.

The method of analysis employed was to fuse 1 to 3 decigrams of the substance for nearly an hour with a large excess, about 3 to 5 grams of a mixture of sodium and potassium carbonates and nitre. Fifteen or twenty minutes' fusion is not sufficient, as ferric phosphate sometimes remains undecomposed. Great care must be taken to reduce the substance to a very fine powder. The contents of the crucible were, after fusion, boiled with water, the ferric oxide was allowed to settle down, the liquid filtered off, and the phosphoric acid in it determined in the usual way.

Of the properties of this compound I have at present little to say, as the little time which I had was taken up in improving the method of preparation, and of the analysis of the compound. It is magnetic. It dissolves slowly in boiling acids, either concentrated or dilute, with evolution of some gas, probably phosphoretted hydrogen and hydrogen. The ignition point of the substance, at least when it is freshly prepared and dry, seems to lie below 100°. When heated in the air, it burns to a reddish brown powder, which appears to contain ferric oxide.

My first object is, however, not to study the properties of this substance, but to apply the same method to the preparation of other phosphides.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Modification of the Optical Saccharometer. By PRAZMOWSKI (Compt. rend., lxxvi, 1212—1214).

IT is easier for some observers to appreciate slight differences of luminous intensity than equally slight differences of tint. Frellet therefore substituted for Soleil's polariser a rhombohedron of calcspar divided across its principal section, the two halves being re-united after removal of a prism of about 2° from each, so that the principal sections are inclined to each other at an angle of 4°. A parallelopiped thus constituted, employed as polariser, furnishes a field of which the two halves are alternately dark in the two positions of the analyser.

Cornu proposed to employ a Nicol's prism cut in the same manner, but the double section is somewhat difficult to execute. The author has attempted to attain the same result more simply by using with a Nicol or other analyser, a thick plate of calcite cut parallel to its axis and divided through the axis, its two halves being re-united after removal of a small angle of about 2° from each. This plate is placed so that the plane of division coincides with the principal section of the prism. Unfortunately the rotatory dispersion of sugar necessitates the employment of monochromatic light, for otherwise the two halves of the field are differently coloured. The author has not been successful in getting a light of sufficient intensity perfectly monochromatic, but the difficulty has been met by using Soleil's quartz compensator.

These modifications may be easily introduced into instruments of the old construction.

W. A. T.

The Spectrum of Erbium. By LECOQ DE BOISBAUDRAN (Compt. rend., lxxvi, 1080—1082).

INCANDESCENT erbia is one of those rare solid substances which produce a brilliant non-continuous spectrum. According to Bahr and Bunsen, the addition of syrupy phosphoric acid augments the brilliancy of the spectral lines, but does not alter their number or position. The author in repeating these experiments arrives at a different conclusion. Having examined the two spectra at the same time, the one placed directly above the other, he finds that the spectrum of erbia is essentially different from that of its phosphate, and inasmuch as a portion of the same sample was used in both cases, no variation in the quality of the erbia can be admitted. The positions and wave-lengths of the bands are tabulated in the original communication. When the flame of the blowpipe is directed upon the anterior face of the phosphate, the spec-

trum is entirely reversed, and black bands are now observed upon a luminous ground. It would appear, therefore, that a transparent layer produces this absorption spectrum, and consequently the luminous spectrum corresponding to it.

The spectra of erbium silicate and borate were also examined, but the experiments are incomplete.

J. W.

The Condensed Discharge of the Induction Spark. By Th. du Moncel (Compt. rend., lxxvi, 1015—1019).

The electric phenomenon to which the author has given the name of "condensed inductive discharge" (*effleuve condensée*), is a peculiar luminous discharge produced by the passage of an induced current between two plates of glass; the plates being separated from each other by an interval not greater than three millimeters, and connected from the outer surfaces respectively with the secondary terminals of a Ruhmkorff coil. Under the influence of the condensation—which is a necessary result from the insulating character of the interposed substance—the molecules of the latter may be supposed to become polarised in a manner similar to those of a liquid electrolyte; they then contribute, individually and separately, in conducting the discharge from one surface to the other of the glass plates. As a result of the peculiar manner in which the transmission is effected, and from the nature of the electrised surfaces, the charge cannot, as in the case of metallic conductors, change its position from one point to another, to take at the moment of discharge the path of least resistance; the condensed discharge differs, therefore, altogether from the direct spark; and inasmuch as the calorific and mechanical effects of the latter are absent, and since the discharge is effected between two unattackable surfaces, the electrochemical effects of which it is capable can be studied with great exactness, all secondary and complex reactions being practically eliminated. The connection with the coil is most satisfactorily made by the intervention of two liquid armatures; and the intensity of the discharge may be made to depend upon the relative dimensions of these armatures and their polarity, being at a maximum when the smaller of the two armatures is positive.

Another arrangement, which indeed is now commonly employed, consists in forming the condenser of two tubes, the one being fitted within the other; the interior armature is formed by filling the interior tube with water, and the exterior by immersing the whole arrangement in a vessel containing water or other suitable medium. The author describes the appearances presented by the discharge under varying conditions, but alludes very briefly to the chemical results obtained by its action, assuming that the researches of Thénard and others are very generally known. The principal object of the communication is to illustrate the difference between the condensed discharge and the direct spark, and to point out the author's personal connection with the subject.

In a short note (*Compt. rend.*, lxxvi, 1082) Thénard remarks, that it

is scarcely just to attribute to M. Jean the credit of priority in illustrating the dissociation of carbonic anhydride under the influence of this new agent, since the latter physicist observed only a small expansion of the gas, and De Saussure had already shown that carbonic anhydride is far from being insensible to the direct spark. His own researches on the contrary had clearly differentiated the discharge in question from the direct spark, and had given a complete solution of the reaction, inasmuch as the gas had been submitted to analysis, and the percentage composition of the resulting products accurately ascertained. He considers that he was the first to demonstrate clearly that the condensed discharge is a new force, since he obtained results by its action which are incapable of being obtained by any other agency.

J. W.

Galvanic Reduction of Iron under the Influence of a Powerful Electro-magnetic Solenoïd. By M. de JACOBI (Ann. Chim. Phys. [4], xxviii, 252).

EXPERIMENTS were instituted with the view of ascertaining whether, in two voltameters traversed by the same current, the quantity of iron reduced was in both cases of equal weight, when, in one voltameter the iron during deposition was submitted to the influence of a powerful electro-magnetic current.

The solution submitted to electrolysis was prepared by dissolving 135 parts of ferrous sulphate, and 123 parts of magnesium sulphate in water, and diluting the liquor to the density 1·27. A Smee's couple furnished the electrolytic current, and the iron was deposited in the form of a tube upon a wax cathode, 34 centimeters long and 2 cm. in diameter, the wax having previously received a very thin coating of electro-deposited copper. Both voltameters were strictly symmetrical in construction, save that one was closely surrounded upon the exterior with a thin cylinder of iron, around which was wound a quantity of covered copper wire. The terminals of the latter were connected with four Bunsen's elements.

After twenty-eight days' action, the deposited iron was examined. The wax having been melted out, the copper was dissolved by a solution of potassium cyanide aided by a weak electric current, and the iron washed and weighed. No. I deposited under magnetic influence, weighed 89·8 grams; No. II 90·7 grams. The difference, 0·9 gram, can therefore be attributed only to experimental error.

The appearance of the two deposits were somewhat different. No. II was fairly smooth and regular. No. I was smooth towards the centre, but at the upper and lower extremities it was characterised by large excrescential growths, which in some places assumed a dendritic or ramose structure. Both specimens possessed a feeble, but only a feeble permanent magnetism.

Electro-deposited iron is naturally hard and brittle, but if it be heated to redness and slowly cooled, it acquires the properties of soft iron, and becomes malleable and ductile. It may be converted into steel by a process analogous to cementation, which communicates to it

the hardness of glass; but by continually heating and cooling a specimen thus hardened, it is brought back to the condition of soft iron.

A tube of galvanic iron is capable of acquiring an intense temporary magnetism, equal to that which can be communicated, under the same conditions, to a solid cylinder of soft iron of the same dimensions; but this magnetism disappears instantly when the magnetizing action ceases, without leaving behind any residual traces, no matter in what manner the magnetic influence was excited.

An induction coil fitted with a galvanic tube will determine physiological commotions notably more intense than those which can be induced by means of a massive cylinder, or of a tube of the same dimensions as the galvanic tube; and it was observed as a fact resulting uniformly from many experiments that, if the wires constituting the central core of an ordinary induction coil be diminished in number, so as to render the shocks comparable with those produced by the galvanic tube, there is a sensible equality between the weights of the wire and of the tube. J. W.

On the Electrical Resistance of Metals. By M. Benoit (Compt. rend., lxxvi, 342—746).

By the determination of the electrical resistance of a number of metals at the boiling temperature of water, of mercury 360°, of sulphur 440°, and of cadmium 860°, the author has been enabled to construct curves and to deduce formulæ expressing the value of the electrical resistance within a very considerable range of temperature.

The metallic wire under examination being at each extremity soldered to a block of copper, was wound upon a cylindrical piece of pipeclay within a narrow deep muffle, which was introduced into a bottle of wrought-iron. This bottle was placed in a gas-furnace with two concentric walls, and its interior was, on the application of heat, raised to the fixed and known boiling temperature of a volatile substance with which it was filled.

The wire was now inserted into one of two equal currents passing in opposite directions round a magnetic needle which was brought back to its original position by inserting an *equivalent* length of wire of known thickness and resistance into the other current.

The following table in which R_0 and R_t express the resistances at 0° and at $t°$, exhibits the increase of resistance with the temperature:

Steel............	$R_t = R_0$	$(1 + 0{\cdot}004978t + 0{\cdot}000007351t^2)$
Iron...............	,,	$(1 + 0{\cdot}004516t + 0{\cdot}000005828t^2)$
Tin...............	,,	$(1 + 0{\cdot}004028t + 0{\cdot}000005826t^2)$
Thallium..........	,,	$(1 + 0{\cdot}004125t + 0{\cdot}000003488t^2)$
Cadmium.........	,,	$(1 + 0{\cdot}004264t + 0{\cdot}000001765t^2)$
Zinc..............	,,	$(1 + 0{\cdot}004192t + 0{\cdot}000001481t^2)$
Lead..............	,,	$(1 + 0{\cdot}003954t + 0\ 000001430t^2)$
Aluminium........	,,	$(1 + 0{\cdot}003876t + 0{\cdot}000001320t^2)$
Silver............	,,	$(1 + 0{\cdot}003972t + 0{\cdot}000000687t^2)$
Magnesium........	,,	$(1 + 0{\cdot}003870t + 0{\cdot}000000863t^2)$
Copper...........	,,	$(1 + 0{\cdot}003637t + 0{\cdot}000000587t^2)$

Gold..............	$R_t = R_0$	$(1 + 0{\cdot}003678t + 0{\cdot}000000426t^2)$
Silver	,,	$(1 + 0{\cdot}003522t + 0{\cdot}000000667t^2)$
Palladium	,,	$(1 + 0{\cdot}002787t + 0{\cdot}000000611t^2)$
Platinum..........	,,	$(1 + 0{\cdot}002454t + 0{\cdot}000000594t^2)$
Brass	,,	$(1 + 0{\cdot}001599t)$
Aluminium bronze..	,,	$(1 + 0{\cdot}001020t)$
Maillechort........	,,	$(1 + 0{\cdot}000356t)$
Mercury	,,	$(1 + 0{\cdot}000882t + 0{\cdot}000001140t^2)$

R. S.

On the Effects Produced by Electric Currents on Mercurial Electrodes Immersed in Various Solutions. By T. du Moncel (Compt. rend., lxxvi, 1136).

In previous papers on this subject, the secondary currents produced when mercurial electrodes are used for the electrolysis of a solution of sodium chloride or potassium cyanide, were attributed principally to the recombination of the gases liberated at the electrodes; but the author now finds that an amalgam of potassium or sodium is formed at the negative electrode, and that the secondary currents are chiefly due to the oxidation of the alkali-metal.

The energy of the secondary current depends on the oxidability of the metal combined with the mercury, the facility with which it unites with mercury, the stability of its salts, and the concentration of the solution. The duration of the secondary currents appears to be related to the time of electrolysis, and to depend on the various circumstances which influence the amount of alkali-metal united with the mercury. The strength of the secondary current is, at first, about the same, whether the electrolysis has lasted for five or for fifteen minutes, but after the primary current has been interrupted for five or ten minutes, a considerable difference may be noticed.

When the electrodes consist of an unoxidisable material, a substance which is not metallic but which can nevertheless call forth energetic chemical action is sometimes deposited at the negative electrode. For example, a solution of sal-ammoniac when electrolysed with a platinum plate as a negative pole, yields a strongly adherent, brownish deposit on the platinum, a secondary current of considerable intensity but very short duration being also produced.

When a small proportion of a salt yielding a powerful secondary current on electrolysis is introduced into a solution capable of yielding only a feeble current, a mixture is obtained which yields a secondary current of considerable energy. For example, a solution of mercury sulphate yields a very weak secondary current when it is electrolysed with mercury as a negative electrode; but if a small proportion of zinc sulphate or sodium bicarbonate be added a secondary current of considerable strength is obtained after electrolysis. This explains the fact that mercury sulphate batteries which only polarise to a small extent when newly charged, become very inconstant after having been in use for some time.

When mercury is used as the positive electrode, energetic secondary currents are produced, which appear to arise from the oxidation of the

mercury and the subsequent reduction of the salts formed; these secondary currents do not last so long as those produced when the negative electrode consists of mercury.

A comprehensive table gives the strength and rate of decadence of the secondary currents produced by electrolysing various solutions. Some of the determinations were made with mercury as a positive electrode, some with this metal as a negative electrode, and others with platinum as a negative electrode.

T. B.

On Thermodiffusion of Gases. By W. Feddersen (Pogg. Ann., cxlviii, 302—311).

When a limited portion of a gas contained in an infinitely long tube is in a state of greater density than the rest, and is heated unequally at the two ends, a continuous motion of the gas will set in, which in the denser portion is directed from the colder to the warmer end. This theoretical result, deduced by Carl Neumann, has been verified experimentally by the author, who obtained a greater density of the gas in one portion of a glass tube by introducing a plug of some gas-absorbing substance, as spongy platinum or palladium, plaster of Paris, charcoal, or magnesia usta.

In one case a plug of spongy platinum 31 mm. long was placed in a glass tube $12\frac{1}{2}$ mm. wide, each end of which was connected with a narrower glass tube $3\frac{1}{2}$ mm. wide; a drop of sulphuric acid placed in each of these tubes indicated the movement of the gas column as soon as the two ends of the platinum plug were heated unequally. When, for instance, one end of the plug was heated to 200°, whilst the other one was freely exposed to the cooling action of the air, the temperature of which was 8°, the following results were obtained:—

Time.	Cold side. Observed.	Cold side. Motion in 10 seconds.	Warm side. Observed.	Warm side. Motion in 10 seconds.
h. m. h. m.				
12 0 until 12 10	225 mm.	225 mm.	beyond the tube	—
12 10 „ 12 15	94 „	188 „	95 mm.	190 mm.
11 15 „ 12 25	no tube	—	211 „	211 „
12 25 „ 12 30	105 mm.	210 „	95 „	190 „
12 30 „ 12 35	110 „	220 „	beyond the tube	—

As all the other substances gave similar results, it appears to be a general fact that porous substances used as diaphragms have the property to draw gases through them from the cold towards the warm surface. Exactly the reverse of this phenomenon, which is called thermodiffusion, takes place in the diffusion of two different gases through a porous diaphragm, as a rise of temperature is observed on that side of the diaphragm where the gas with the greater power of diffusion enters.

R. S.

A New Siphon. By JOS. SEDLACZEK (Pogg. Ann., cxlviii, 333). Not easily described without figures.

Diffusion of Gases through Porous Walls, and the accompanying Changes of Temperature. By L. DUFOUR (Pogg. Ann., cxlviii, 490—492).

1. *Diffusion of Two Gases under Constant Pressure.*—On that side of the porous wall at which the gas diffuses inwards, there is an elevation of temperature, accompanied by a lowering of temperature at the other side. This the author supposes to be due to a partial condensation of the gas on the porous substance in the one instance, and to a partial rarefaction in the other.

2. *Diffusion with Change of Pressure.*—When one gas diffuses into a porous vessel which already contains another gas (as hydrogen into a vessel containing air), there is a slight elevation of temperature, accompanied by an increase of pressure. As the first gas diffuses out, the thermometer falls until a point is reached at which it again begins to rise. The author also finds that dry air diffuses into air which is relatively wetter than itself; this phenomenon is accompanied by the same changes of temperature as already noticed in the case of two gases.

M. M. P. M.

The Constitution of the Hydracids in Solution, and their Inverse Reactions. By M. BERTHELOT (Bull. Soc. Chim. [2], xix, 385—393).

IN examining the constitution of the liquids resulting from the union of the hydracids with water, the author has availed himself of the indications afforded by the heat produced on dilution, whose progressive increase with the proportion of water shows the existence of a group of definite hydrates represented by the formulæ—

$$HCl + 8H_2O \quad HBr + 4H_2O \quad HI + 4H_2O.$$

A second method was to observe when a current of carbonic anhydride passed through the solutions, ceased to carry off sufficient acid to give any precipitate with argentic nitrate. The limit at 12° corresponds with acids of the composition—

$$HCl + 6{\cdot}5H_2O \quad HBr + 4{\cdot}2H_2O \quad HI + 4{\cdot}7H_2O,$$

agreeing closely with the results obtained by Bineau and also by Roscoe and Dittmar. These hydrates, however, do not seem to be definite combinations, as small quantities of acid are carried off by the current of gas even when much more largely diluted. As it appears, from the experiments of Roscoe and Dittmar, that the difference in composition of the hydrated acids boiling at constant temperatures under pressures varying from 0·05 to 2·50 meters, does not vary greatly, being from $HCl + 6{\cdot}7H_2O$ to $HCl + 9{\cdot}3H_2O$; $HBr + 4{\cdot}2H_2O$ to $5H_2O$; $HI + 4{\cdot}7H_2O$ to $5{\cdot}5H_2O$, the author concludes that they are mixtures of at

least two definite hydrates, one of which is stable, whilst the other, the least hydrated, is in a state of partial dissociation varying with the temperature. It is, moreover, the anhydrous acid, and not a definite hydrate which volatilises below the limit of stability, for hydrobromic acid gas, saturated with the vapour of water, gives the same calorific results on solution as perfectly dry gas.

It would seem, therefore, that concentrated solutions contain a certain amount of anhydrous acid, whose proportion at a given temperature can be calculated, the solutions being mixtures of the hydrates with the anhydrous acid simply dissolved, that is to say, liquefied in them. The precipitation of saturated solutions of the alkaline chlorides by hydrochloric acid also serves to control the state of hydration of these liquids, the acid taking from the solution of the salt the water necessary to convert it into a stable hydrate. The limit when it ceases to precipitate the salt is $HCl + 7\cdot5H_2O$ with potassium chloride; $HCl + 6H_2O$ with sodium chloride; $HCl + 5H_2O$ with ammonium chloride, and $HCl + 9H_2O$ with barium chloride, the difference in these results being due principally to the greater or lesser solubility of the salt in hydrochloric acid. The author considers that the results of these determinations establish the existence of a certain amount of anhydrous acids in concentrated solutions of the hydracids.

The great value of the study of the constitution of the hydracids in solution is, that it seems to play an important part in chemical reactions, especially those in which the action varies with the concentration of the solution, as for example, in the evolution of sulphuretted hydrogen on treating native antimony sulphide with concentrated hydrochloric acid, and the inverse reaction of the precipitation of sulphide of antimony by sulphuretted hydrogen from a solution of antimony chloride in dilute hydrochloric acid; the neutral point here corresponds, at the ordinary temperature, with an acid of the strength $HCl + 6H_2O$. An acid somewhat more concentrated than this attacks native sulphide of antimony with disengagement of sulphuretted hydrogen, but on adding a small quantity of water to the liquid, which now contains both antimony chloride and sulphuretted hydrogen in solution, an orange-coloured precipitate of the sulphide immediately makes its appearance. This forms an admirable lecture experiment. The action of concentrated hydrochloric acid on the antimony sulphide is accompanied by a sensible absorption of heat due to the formation of the gaseous sulphuretted hydrogen; this absorption being less than the heat of solution of the gas.

In the energetic reducing action exerted by concentrated hydriodic acid, it is really the anhydrous hydracid dissolved which produces the effect "by virtue of the excess of energy it possesses compared with its definite hydrates," that is, the heat corresponding to the transformation of the anhydrous acid contained in the solution into certain stable hydrates. A similar explanation may be given of the inverse action of concentrated hydriodic acid on sulphur, producing sulphuretted hydrogen, and of sulphuretted hydrogen on iodine in presence of a large amount of water. forming hydriodic acid, the neutral point appearing to correspond with an acid of the strength indicated by the formula $HI + 7H_2O$, which is the same as for the inverse actions of concen-

trated sulphuric acid on concentrated hydriodic acid, and of sulphurous anhydride on iodine in presence of water.

Thus it is proved that dilute solutions of the hydracids contain only definite and stable hydrates, whilst concentrated solutions contain at the same time hydrates in a state of dissociation, and also a certain proportion of anhydrous acid. In the phenomena of inverse chemical reactions produced by these two kinds of solutions, it is the anhydrous acid which effects certain reactions, whilst the hydrates are either indifferent or even produce an inverse action.

C. E. G.

A new Form of Aspirator. By H. LASNE (Bull. Soc. Chim. [2], xix, 291—295).

THIS apparatus is founded on the well-known mechanical principle called the diverging jet. When water is made to flow through a pipe the diameter of which continually increases from above downwards, the same quantity of water passes in any given time through the two extreme sections, but in passing from the first to the second, it has lost a part of its velocity. This loss is necessarily due to a force which opposes the movement of the liquid, and, neglecting friction, the only force that can produce this effect is the difference of the pressures at the two sections under consideration. The pressure must therefore vary from one section to the other, and must be least where the velocity is greatest, that is to say, at the narrow section. At the wide end of the diverging tube the water is exposed to the pressure of the atmosphere; and if the circumference of the narrowest portion be made to communicate with a barometer tube, the mercury will rise in the tube to a height depending on the ratio of the two sections.

The body of the author's apparatus consists of a chamber with three openings, one at the top, one at the bottom, and a lateral one. To this last is fitted the tube which is in communication with the air to be aspired. In the opening at the top, a tube, placed in communication with a tap capable of delivering water at a pressure equal to a fall of 18 meters, slides up and down in a stuffing-box. To the lower opening is fitted a conical efflux-tube, with its large end downwards. When the water is flowing, the upper tube is so adjusted that the *vena contracta* may occur just within the narrow part of the efflux-tube and draw away the air from the body of the instrument, and so, by the lateral tube, from any vessel placed in communication with it. The lateral tube has a valve which prevents the water from entering the vessel to be exhausted, and also serves to maintain the vacuum. The author does not give any dimensions, but from the diagram of the apparatus the conical efflux-tube would appear to be about 80 mm. in length, 2 mm. in diameter at the small end, and 8 mm. diameter at the large end. The influx-tube is about 8 mm. in diameter at the top, and rather less than 2 mm. where the water leaves it, and the lateral tube is about 4 mm. in diameter; the above are all interior measurements. The amount of water issuing per minute is from 2 to 3 litres. As to the extent of the vacuum produced, the air left in a bell-jar containing 7 litres will sustain 24 mm. of mercury after the apparatus has been exhausting it for an hour. After an hour and a half the vacuum would

be 15 mm. This limit cannot be passed. The apparatus would appear to be very useful in cases where the Bunsen pump cannot easily be employed, *e.g.*, at the bottom of a house. B. J. G.

The Hydrates of Monobasic Acids. By A. GEUTHER (Deut. Chem. Ges. Ber., vi, 403—405).

GRIMAUX has lately shown (this Journal, 1873, 371), that the hydrates of the fatty acids have to be considered as "atomic compounds." The author now points out that he has expressed similar views in his *Lehrbuch*, published in 1869. The hydrates of other acids have likewise a similar constitution; thus the hydrate $NO_3H + 2H_2O$ is perhydroxyl-nitric acid $N(OH)_5$, &c. C. S.

Thermo-chemical Investigations, xi—Affinity of Hydrogen for the Non-metallic Elements, Chlorine, Bromine, Iodine, Oxygen, Nitrogen, and Carbon. By J. THOMSEN (Pogg. Ann., cxlviii, 177—203 and 368—404).

THE results of this investigation have already been given in this Journal, 1872, p. 215, and 1873, p. 126. The present paper gives a description of the apparatus employed, with full details of the mode of experimenting and working out the numerical results.

Calometric Researches on the State of Bodies in Solutions. By M. BERTHELOT (Ann. Chim. Phys. [4], xxix, 94—186).

THIS is the first of a series of papers giving the details of M. Berthelot's researches on the above subject. The results have been already given in this Journal, 1871, pp. 975, 982, 1129; 1872, 19, 21, 107, 212, 875; 1873, 236, 468. The present paper contains the description of the calorimetric apparatus and methods employed.

On the Internal Friction of Gases—Fifth Memoir; Influence of Temperature on the Friction. By O. E. MEYER (Pogg. Ann., cxlviii, 203—236).

Conduction of Heat in Crystallised Bodies. By E. JANNETAZ (Ann. Chim. Phys. [4], xxix, 5—82).

On the Molecular Rotation of Gases. By G. HINRICHS (Compt. rend., lxxvi, 1357—1360).

On the Vapours emitted at a given Temperature by the same Body under Two Different States. By J. MOUTIER (Compt. rend., lxxvi, 1074—1077).

Reply to Berthelot's Last Note on the Mercury Calorimeter. By P. A. FAVRE (Ann. Chim. Phys. [4], xxix, 82—86).

On the Theory of Sun-spots and on the Dark Nucleus of the Sun. By E. VICAIRE (Compt. rend., lxxvi, 1396—1399).

Researches on the Production of Electricity by Mechanical Actions. By L. JOULIN (Compt. rend., lxxvi, 1299—1303).

Action of Electricity on Flames. By V. NEVRENEUF (Compt. rend., lxxvi, 1000).

Comparison of Different Electrical Machines. By M. MASCART (Compt. rend., lxxvi, 1011—1014).

On the Electric Balance and an Electrostatic Phenomenon. By P. VOLPICELLI (Compt. rend., lxxvi, 1296—1299).

On the Resistance of Galvanometers. By J. RAYNAUD (Compt. rend., lxxvi, 1014).

On the Conditions of Maximum Magnetic Effect in Galvanometers and Electro-magnets. By J. RAYNAUD (Compt. rend., lxxvi, 1303).

Inorganic Chemistry.

Remarks on Fudakowsky's Paper on Active Oxygen.

By E. SCHAER (Deut. Chem. Ges. Ber., vi, 406—410).

THE slow oxidation of hydrocarbons and the simultaneous formation of ozone takes place, not only by insolation, but also by heat within certain limits of temperature. When the oils of turpentine, juniper, lemon, &c., are distilled with water in presence of a large volume of air, the distilled water, as well as that remaining behind, shows the reaction of hydrogen peroxide, whilst the distilled oil contains ozone. Several oils containing oxygen behave in a similar way, and also the benzene- and petroleum-hydrocarbons, only they require repeated distillation and a very large volume of air. As some of the ozone is destroyed again at the boiling point, better results are obtained by heating the oils in a constant current of air.

The author believes that when these hydrocarbons are slowly oxidised, a part of the oxygen is converted into ozone, whilst another part combines with the hydrocarbon in a peculiar way (Schoenbein's organic antozonide). This antozone oxidises the hydrocarbon, but much more slowly than ozone, and is easily removed by treating the oils with ozonides (potassium permanganate, lead peroxide, &c.), whilst barium peroxide and other antozonides do not act on it. Oils containing the two modifications of oxygen show the ozone-reactions much more strongly on addition of hæmoglobin, diastase, ferrous oxide, platinum-black, and other ozone-carriers. If such an oil is shaken with acidulate water, hydrogen peroxide is formed, and if this treatment is continued until the water does not show the reactions of the peroxide, the oil still gives the reactions of ozone, but the ozone-carriers no longer make them more intense. This shows that the antozone has been removed as hydrogen peroxide, whilst the ozone is left behind.

C. S.

Action of Oxygen Dissolved in Water on Reducing Agents. By P. SCHÜTZENBERGER and C. RISLER (*Compt. rend.*, lxxvi, 1214—1216).

WHEN a solution of sodium hyposulphite (Schützenberger's hydrosulphite) titrated by means of ammoniacal copper sulphate is added to aërated water tinted with indigo, the indigo is decolorised when a quantity of the liquid has been added sufficient to consume just half the oxygen present. The liquid thus decolorised becomes blue again under the influence of the slightest trace of free oxygen, and the gases extracted from it by ebullition or by the mercurial pump consist of nitrogen and carbonic anhydride without appreciable traces of oxygen.

If an excess of a colourless solution of ammoniacal cuprous chloride is added to aërated water the liquid becomes blue, and on titrating by means of hyposulphite, the cupric oxide which has been formed, it is found that this corresponds precisely to the half of the dissolved oxygen. These experiments were all conducted in an atmosphere of pure hydrogen.

From various experiments the authors are led to conclude that certain reducing agents, notably sodium hyposulphite and ammoniacal cuprous chloride in presence of oxygen dissolved in water, divide the oxygen into two equal parts, one of which acts upon the reducing agent itself, the other remaining disguised in the liquid. Stannite of sodium, however, removes the whole of the dissolved oxygen. The authors think it probable that the oxygen which thus disappears produces with the water hydrogen peroxide. It becomes free again on heating the liquid, and this observation has led to a modification of the process of titration by which the whole of the dissolved oxygen is obtained.

In operating upon bullock's blood saturated with oxygen, the authors find that it contains from 24 to 28 per cent. of oxygen, or 5 to 9 per cent. more than the quantity capable of extraction by the pump.

W. A. T.

The Purification of Hydrochloric Acid. By ENGEL (*Compt. rend.*, lxxvi, 1139).

IN order to remove arsenic from hydrochloric acid, the author recommends an addition of four or five grams of potassium hypophosphite to each litre of the acid; the arsenic soon becomes reduced, and when it is all deposited the clear acid can be decanted and distilled.

Potassium hypophosphite can be used as a test for the presence of arsenic in hydrochloric acid, the reduction taking place immediately on the application of heat.

T. B.

New Process for the Preparation of Sulphuretted Hydrogen as a Laboratory Reagent. By W. SKEY (*Chem. News*, xxvii, 161).

IT is proposed to supersede the ordinary process for the preparation of sulphuretted hydrogen by the following. The generating flask is

charged with fragments of galena and granulated zinc in about equal proportions, and the mixture covered with dilute hydrochloric acid (1 to 20). An energetic and regular current of sulphuretted hydrogen is evolved. The gas is accompanied by a little free hydrogen, and requires washing to remove traces of hydrochloric acid.

The apparatus may also be arranged as a simple galvanic couple, in which a piece of *massive* galena occupies the position of the negative element; the connecting wires are passed through the cork of the apparatus, and are brought into contact with each other by means of binding screws. The evolution of gas commences on making the connection, and ceases instantly when the current is interrupted. This latter arrangement, though somewhat more troublesome to prepare, is nevertheless to be preferred, inasmuch as it avoids the necessity of removing the exciting liquid when the evolution of gas is no longer required.

J. W.

Contributions to the Knowledge of Monochlorosulphuric Acid.
By MAX MÜLLER (Deut. Chem. Ges. Ber., vi, 227—231).

AFTER giving a summary of the investigations of Williamson, Baumstark, and Williams of this substance, the author remarks that it may possibly exist under two isomeric forms, Cl—S—O—O—OH and HO—S—O—O—Cl. In order to determine which formula belongs to the ordinary chlorosulphuric acid, he examined the salts and ether of the acid, but as the former did not yield very satisfactory results, his attention was more particularly directed to the ether.

Ethylene is readily absorbed by the acid, yielding a liquid which may be purified by distillation under diminished pressure, passing over almost entirely between 93° and 95° at 100 mm. It is a colourless, mobile liquid which fumes when exposed to the air, and possesses a pungent odour, producing a copious flow of tears. It is heavier than water, being slowly decomposed by it in the cold and rapidly when heated, with formation of hydrochloric acid, sulphuric acid, and alcohol. Hot aqueous potash and cold alcoholic potash readily decompose it, ethyl chloride being evolved and potassium sulphate formed. It dissolves without decomposition in pure ether, but with alcohol or amylic alcohol it evolves ethyl chloride, ethylsulphuric acid or amyl sulphuric acid being simultaneously produced.

Of the two isomeric formulæ belonging to ethyl chlorosulphate,

$$C_2H_5O—S—O—O—Cl$$
$$Cl—S—O—O—OC_2H_5,$$

the first would be the chloride of ethylsulphuric acid, and must be decomposed by water into ethylsulphuric acid and hydrochloric acid; the second therefore represents the composition of ethyl chlorosulphate, and the acid itself will have the formula—

$$Cl—S—O—O—OH.$$

The author has also examined the action of sulphuric anhydride on ethyl chloride; the oily product obtained cannot be distilled without

decomposition and consists of two compounds, one of which is insoluble in water and is identical with the ethyl chlorosulphate already described. The aqueous solution of the other, after separation of the hydrochloric acid and sulphuric acid, was found to contain a substance which easily decomposed, with formation of isethionic acid. The author was unable to isolate this new compound, but believes it to be a product of the action of sulphuric anhydride on ethyl chlorosulphate, a supposition confirmed by the results obtained on treating pure ethyl chlorosulphate with sulphuric anhydride. He concludes with some observations on the isethionates. The *barium salt* crystallises from 65 per cent. alcohol in large transparent crystals; the *potassium salt* from 80 per cent. alcohol in needles which melt at 190° and not at 300°—350°, the temperature usually given.

C. E. G.

The Preparation of Phosphonium Iodide.

By A. W. HOFMANN (Deut. Chem. Ges. Ber., vi, 286—292).

SERULLAS prepared phosphonium iodide from a mixture of iodine and phosphorus moistened with water. H. Rose substituted hydriodic acid for water.

Baeyer dissolves 100 grams of phosphorus in carbon sulphide, and adds 175 grams of iodine, and after removal of the sulphide 50 grams of water very gradually.

Owing to the increased use of phosphonium iodide in chemical researches, it seemed desirable to examine these methods, and to find the best means of preparing the substance in quantity.

The proportions recommended are 100 parts of phosphorus, 170 parts of iodine, and 60 parts of water; but Hofmann prefers to work with four times the above weights. Phosphorus (400 grams) is dissolved (in a retort of one-litre capacity) in its own weight of carbon sulphide, and after complete cooling the iodine (680 grams) is added little by little. The carbon sulphide is then carefully distilled off in the water-bath. The retort is next gently warmed, and the water (240 grams) allowed to flow in very slowly. A stream of carbonic acid is made to flow through the apparatus during the operation. Further details can scarcely be given without reproducing the woodcut by which the paper is accompanied.

G. T. A.

Arsenetted Hydrogen.

By J. V. JANOWSKY (Deut. Chem. Ges. Ber., vi, 216—220).

WHEN dry arsenetted hydrogen is passed over phosphorus trichloride kept cool, hydrochloric acid is evolved and *arsenic phosphide*, PAs, is deposited.

Arsenic phosphide when first deposited, possesses a bright reddish-brown colour, but on drying it becomes dark and lustreless. It is insoluble in alcohol, ether, and chloroform, but dissolves slightly in carbon sulphide. Cold sulphuric acid and hydrochloric acid have no action on it, but the application of heat appears to cause partial solu-

tion. Concentrated nitric acid oxidises it, with production of flame, and the same acid when dilute and warm oxidises it readily to arsenic acid and phosphoric acid. Potash-solution, ammonia, and baryta-water decompose it slowly in the cold, and more rapidly on the application of heat, phosphoretted hydrogen, arsenetted hydrogen, phosphorous acid, arsenious acid, and metallic arsenic being produced. After long heating, the solution contains phosphoric acid and very little arsenious acid, the greater portion of the arsenic having separated in the metallic state. When arsenic phosphide is heated, it burns to arsenious anhydride and phosphoric anhydride, and when it is heated in a closed vessel it is decomposed, the phosphorus subliming before the arsenic. The author did not succeed in obtaining this substance in a definite state by the direct action of phosphorus on arsenic, but it is formed when phosphoretted hydrogen is made to act on arsenic trichloride. When arsenic phosphide is treated with water, a substance having the composition $As_3P_2O_3$ is obtained. This substance is not much acted on by acids, with the exception of nitric acid. With alkalis it reacts like arsenic phosphide, but a considerable quantity of arsenic is set free even in the cold. It is decomposed slowly when heated to 100°, and rapidly at 250° C.

The arsenic phosphide which Pelletier obtained by fusing together phosphorus and arsenic under water was found by the author to yield up its phosphorus to carbon sulphide.

When arsenetted hydrogen comes in contact with concentrated sulphuric acid, hydrochloric acid, or moist hydrochloric acid gas, metallic arsenic is deposited, and this deposited arsenic dissolves in sulphuric acid on the application of heat, sulphurous acid being evolved.

Arsenic trichloride when treated with arsenetted hydrogen is decomposed, metallic arsenic and hydrochloric acid being produced.

The arsenetted hydrogen employed in the above experiments was prepared by the action of dilute acid on sodium arsenide, this being obtained by heating sodium in the impure gas evolved when arsenical zinc is treated with dilute acid.

The solid residues obtained by treating metallic arsenides with acids have been usually regarded as arsenides of hydrogen; the author, however, finds that these residues often consist of metallic arsenic. When pure sodium or potassium arsenide is treated with water, a brown velvety residue having the composition AsH is obtained.

T. B.

Action of Sulphur upon Arsenic. By A. GÉLIS (Compt. rend., lxxvi, 1205—1209).

WHEN sulphur and arsenic are fused together, the products vary according to the relative proportions of the two bodies, but such products are definite, few in number, and easily determined. Sulphur heated with excess of arsenic forms but one product, viz., arsenic bisulphide, which is opaque, of a coral-red colour, and has a crystalline fracture.

When the sulphur is in excess, a mixture is obtained consisting of arsenic, pentasulphide, and sulphur. Liquid ammonia will dissolve out

the pentasulphide and leave the sulphur. Or if the mixture be distilled in an earthenware retort, sulphur is the first product, then a mixture of sulphur and arsenic, and the residue in the retort consists of arsenic pentasulphide. If the distillation be continued, the pentasulphide decomposes into sulphur and arsenic trisulphide, and the latter may be distilled without decomposition.

The mixture of sulphur and arsenic which distils over after the sulphur, when treated several times with carbon sulphide yields a product which the author found to contain from 9·27 to 11·41 equivalents of sulphur to one of arsenic. It is therefore suggested that this compound may be represented as AsS_{10}, or that it may be considered as arsenic pentasulphide in which the molecule of sulphur has been formed by the condensation of two molecules of ordinary sulphur.

When sulphur and arsenic are heated together in proportions within the limits indicated by their two extreme compounds, mixtures of di-, tri-, and pentasulphide are obtained according to the quantity of each used, the trisulphide being either formed directly or from the decomposition of the pentasulphide.

J. B.

Note respecting the Decomposition of Metallic Carbonates by Heat. By L. Joulin (Bull. Soc. Chim. [2], xix, 345—354).

The carbonate submitted to examination was placed in a suitable glass tube and the latter connected with a manometer and mercurial pump. The salt was dried at a low temperature in an atmosphere of carbonic anhydride, and the tube having been exhausted, was then heated by immersing it in an oil-bath.

Manganese carbonate began to decompose at 70°. At 150° the tension of the carbonic anhydride attained a certain value, 215 mm., which remained constant for that temperature; when the salt was allowed to cool, recombination took place, and the tension reverted slowly to its initial value. Above 200° decomposition began to be complete, and the elastic force of the gas augmented constantly to two atmospheres; the carbonate became brown in colour, and little or no reabsorption took place on cooling.

It was observed, when the carbonate was heated to 100°, 150°, 200°, and allowed to cool, that on raising the temperature a second time to 100°, the extreme tension was less than one-half of the tension attained when the salt was heated for the first time to 100°, and that a third heating produced no sensible alteration of the lower tension. Since no exhaustion was effected during the three operations, the author is of opinion that the phenomenon can only be explained by assuming some intermolecular change in the carbonate to have taken place, which has rendered the body more stable, and consequently more able to resist decomposition at low temperatures. This explanation is also strengthened by the fact that when the temperature of the bath was rapidly raised, the elastic force of the gas attained a value, 489 mm., more than double of that at which it remained constant after a lengthened heating, 215 mm.; a circumstance which seems to imply that the molecules are not, in the first instance, in that condition of stable equilibrium which

they finally acquire when the temperature has passed a certain degree, and remained uniform for a considerable time.

The results of the experiments with silver carbonate were somewhat different from those with manganese carbonate, inasmuch as the decomposition of the carbonate and resulting oxide proceeded simultaneously at temperatures above 200°. Below this, the extreme tension was sensibly inferior to that of manganese carbonate under the same conditions, and the salt altogether underwent decomposition with greater facility.

The decomposition was complete at 225°.

Experiments with lead carbonate gave similar results.

The object of these investigations was to show that the composition of the carbonates and hydrocarbonates of these and similar metals cannot be satisfactorily ascertained, unless great precautions are taken in the preparation and drying, &c., of the material submitted to analysis.

J. W.

Reactions of various Metallic Salts. By J. Myers (Deut. Chem. Ges. Ber., vi, 440).

O. Loew has examined the action of potassium sulphide on copper sulphate; the author has examined the same action in the case of nickel chloride, nickel sulphate, mercurous nitrate, cobalt chloride, ferrous sulphate, mercuric chloride, and lead acetate, which are all reduced to the metallic state (like copper sulphate), potassium polysulphide being formed. Zinc sulphate gives zinc sulphide; silver nitrate, a thin pellicle of silver sulphide, with a thinner underlying film of silver. Potassium iodide gives no results, saving a heteromorphous lead iodide, with lead acetate. Yellow potassium chromate becomes dichromate in contact with copper sulphate, silver nitrate, mercurous nitrate, and mercuric chloride. With copper sulphate, a brown crust of basic copper chromate is formed; with the mercurous salt, a crystalline layer of basic nitrate, covered with a film of mercurous chromate; with mercuric chloride, a covering of red chromate is formed, a yellow layer being underneath, probably an oxide or basic salt. Lead acetate is unchanged, and cobalt chloride completely precipitated.

Solution of potassium ferricyanide brought into contact with ferrous sulphate, gives a green fluid smelling of hydrocyanic acid; three layers are formed on the crystals, one of Turnbull's blue, another (green) probably of ferrous ferrocyanide, a third of iron hydrate. Copper and zinc sulphates produce ferricyanides.

C. R. A. W.

An instance of Stability of Silver Chloride in Sunlight. By F. Field (Chem. News, xxvii, 175).

A variety of silver from Bolivia, containing silver 78·12, silver chloride 12·01, ferric oxide 9·34, cobalt 0·40, was very brittle, owing, the author thinks, to the presence of the chloride (see this Journal [2],

ix, 498, 666). When the chloride was exposed to sunlight, it blackened, but when the metallic silver in the mineral was dissolved in nitric acid, and precipitated as chloride, the washed precipitate did not blacken when exposed to sunlight for many days. Another instance of stable silver chloride is mentioned in this Journal, x, 242.

B. J. G.

On some New Compounds of Indium. By C. ROESSLER (J. pr. Chem. [2], vii, 14—15).

THE atomic weight of indium deduced from the specific heat of the metal requires the formula of the oxide to be written, In_2O_3, and the formulæ of other compounds in a corresponding manner. The compounds of indium hitherto studied are not characterised by properties confirming with certainty the correctness of these formulæ. The author has, however, now discovered such a compound in indium-ammonium alum. This body was obtained by evaporating over the water-bath solutions of indium and ammonium sulphates, mixed in the proportion of their molecular weights. The concentrated solutions, on standing in the cold, deposited transparent octohedral crystals, which, when analysed, gave numbers corresponding with the formula, $In_2O_3.(NH_4)_2O.4SO_3 + 24H_2O$, or $In'''(NH^4)(SO^4)^2 + 12H^2O$.

All attempts to obtain indium-sodium and indium-potassium alum failed.

Indium ammonium alum crystallises easily in large octohedrons, always exhibiting the cube-faces. It appears to undergo fusion at 36°, but really breaks up into a solution of the alum and a salt containing less water (see below). The liquefied mass, when examined with the microscope, is seen to contain monoclinic prisms of the latter salt, whilst octohedral crystals of the alum are again formed, as it cools. This breaking up takes place even on triturating crystals of the alum with a pestle, the result being not a dry powder, but a moist pasty mass. The alum is very soluble in water, 1 part of water dissolving 2 parts of alum at 16°, and about 4 parts at 30°. It is insoluble in alcohol. The strongly acid aqueous solution deposits on boiling a white powder, corresponding in composition to alum-stone, and having similar properties.

The formation of the above-mentioned salt with less water takes place, as it evidently must do, when a solution of the alum is made to crystallise at 36°. Thus formed, it was found to have the composition represented by the formula, $In_2O_3.(NH_4)_2O.4SO_3 + 8H_2O$. Corresponding salts were obtained with potassium and sodium sulphates.

J. R.

Lead: its Impurities, and their Influence on the Technical Use of the Metal. By G. BRIGEL (Deut. Chem. Ges. Ber., vi, 191).

IMPURE lead is usually somewhat whiter and less soft than pure lead, which readily stains the hands, linen, &c. Sulphur, iron, tin, antimony, and copper are the usual impurities, and are injurious for many

technical applications, especially white lead making. Pure lead melts at 330°—335°; at a little below the melting point it is brittle; at a white heat it is volatile in closed vessels.

C. R. A. W.

Affinity in Solutions of Ferric Chloride. By A. MÜLLER (Pogg. Ann. Erganzungs-band, vi, 123—141).

THE author has studied the effect of dilution in changing the colour of a ferric chloride solution.

The specific intensity of the colour (*i.e.*, the intensity calculated from a known quantity of iron employed) depends upon—

1. The nature of the diluent.
2. The temperature of the solution.
3. The age of the solutions.

1. The intensity of the colour of a feebly acid ferric chloride solution decreases by dilution with *water* more rapidly than in a strictly inverse proportion to the increase of volume.

Hydrochloric acid generally increases the specific intensity, but by using a ferric chloride solution of a particular degree of concentration the intensity is unchanged on addition of this acid.

Ammonium chloride has an effect similar to hydrochloric acid, one atom of this salt having the same effect as two-thirds of an atom of the acid.

Ammonium chloride and hydrochloric acid together increase the intensity more than the sum of the two separately, in the proportion of 9 to 8.

Three atoms of *sodium chloride* have an effect equal to five atoms of hydrochloric *acid*.

2. Increase of temperature increases the intensity, a rise of 30° causing an increase in the proportion of 1 to 1·4 or 1·5.

3. Some time must elapse before the solution, diluted or raised in temperature, has acquired its minimum or maximum intensity.

The author accounts for these various facts by saying that the ferric chloride undergoes chemical changes. The addition of water causes the anhydrous chloride to be changed into hydrochloride of ferric oxide (Salzsaures oxyd). Addition of hydrochloric acid hinders this change, because it increases the points of contact between the atoms of iron and chlorine. Sodium and ammonium chlorides form stable chlorine-compounds, and these assist the molecules of ferric chloride to withstand the incursions of the water-molecules. Increase of temperature increases the motion of the iron and chlorine atoms towards one another, and hence their rapidity of combination. Time is required to overcome the *chemical inertia* of the molecules, which, after they have been driven asunder by the influence of some added substance, do not at once settle into their proper positions.

The intensity of colour of pure ferric chloride has not yet been determined. It is somewhat more than double that of ferric acetate. It absorbs more red light than potassium dichromate, and appears more green in shade.

The author has also studied the action of various acids on ferric

chloride, and finds that at temperatures at which acetic acid has no great tension, it is able to displace hydrochloric and sulphuric acids from such weak bases as ferric oxide, but not from strong bases such as the alkalis.

M. M. P. M.

Action of Aluminium on Zinc Chloride. By F. FLAVITSKY (Deut. Chem. Ges. Ber., vi, 195).

ALUMINIUM reduces zinc as regulus from fused anhydrous zinc chloride—

$$3ZnCl_2 + 2Al = Al_2Cl_6 + 3Zn,$$

but does not similarly reduce magnesium chloride. Chloraluminate of sodium, $AlNaCl_4$, is decomposed by water.

C. R. A. W.

Preparation of Chrome Alum. By A. LIELEGG (Dingl. polyt. J., ccvii, 321).

100 PARTS by weight of the alum are produced by adding 29·5 parts potassium dichromate to a warm mixture of 39 parts sulphuric acid diluted with a quantity of water sufficient to dissolve the bichromate, and, when this solution is cool, adding 38 parts of crystallised oxalic acid in small portions at a time. After filtering, the alum crystallises out on standing.

M. M. P. M.

Influence of Acids on Iron and Steel. By W. JOHNSON (Chem. News, xxvii, 176—178).

PIECES of iron and steel wire on immersion in hydrochloric or sulphuric acid, washing in water, and drying, were found to have gained in weight. This gain varied from 0·0005 to 0·06 per cent., being greater with iron than with steel, and with sulphuric than with hydrochloric acid. (The first of the above numbers appears very small, but the author would seem to be in possession of extraordinarily accurate weighing apparatus, since he gives weights of over 80 grams to the $\frac{1}{100}$ milligram. He moreover calculates all percentages to the sixth decimal.) The breaking strain of iron wire was diminished by immersion in hydrochloric acid from 0·5 to 3 per cent., and in the case of steel wire 4·67 per cent. The elongation of iron wire was but little affected by the same treatment, but the elongation of steel was increased about 30 per cent. The toughness of both was diminished, that of steel in a very marked way, a coil of steel, after immersion, breaking if allowed to fall on the ground, and even flying in pieces directly it was placed in the acid. When iron and steel wire which had been immersed were heated in a confined space, the surface became rusted, sometimes uniformly, sometimes in spots. This did not take place if the air had free access. The spotted rust forms in some cases without heating, by mere lapse of time. When the wire, after immersion in acid, washing and

drying, coating with lime, and drawing out finer to remove every trace of acid from the surface, is broken, and the fracture is moistened, bubbles of gas rise over the whole surface of the fracture. The water does not, however, alter litmus-paper. By exposure to air, washing with water, or gentle heating, all the above effects of acid upon iron or steel decrease in intensity and finally cease, leaving the metal in its original state. Pyroligneous acid acts in a similar way to the two acids mentioned. Zinc appears to have a power similar to that of acid in rendering iron brittle. A piece of galvanised iron which could be bent to and fro several times without breaking was rapidly raised to a red heat, so that all the zinc should not be volatilised. On trying to bend it, it broke off short, although when all the zinc was volatilised it could not be broken by bending.

B. J. G.

Mineralogical Chemistry.

Graphite. By J. STINGL (Deut. Chem. Ges. Ber., vi, 391).

GRAPHITE was purified as far as possible by elutriation and repeated treatment with alkali, aqua regia, and hydrofluoric acid, the amount of ash being thus reduced to 0·12 per cent., and in the case of graphite from Bohemia and Styria the amount of ash was diminished still further. Sometimes the ferric oxide present in graphite exists in the soluble state, and sometimes in the insoluble state, and the graphite from Styria frequently contains fragments of readily pulverisable quartz. In purifying graphite an effectual elutriation is of great importance.

When graphite from Bohemia or Styria is carefully purified and converted into graphitic acid, the product forms a yellow amorphous powder, no crystalline structure being visible; and when this graphitic acid is heated, a residue is obtained which decolorises, and possesses a covering power greater than that of lamp-black. Foliated or crystalline graphite yields, on the other hand, a graphitic acid which is crystalline, and the residue obtained by heating it possesses neither decolorising nor covering power. The amorphous graphitic acid obtained from the above-mentioned kinds of graphite, gave satisfactory numbers on analysis, and the author is engaged in studying the graphitic acid obtained from the crystallised graphite deposited during the preparation of crude soda. The graphite from this source was found to contain 79·79 per cent. of carbon, 11·27 per cent. of ferric oxide, and 10·05 per cent. of silica. The presence of ferric oxide in this kind of graphite leads the author to believe that the sodium cyanide and sodium ferrocyanide contained in the crude soda are converted into carbon monoxide, nitrogen, magnetic oxide of iron and sodium hydrate by oxidation, and that the action of carbon monoxide on magnetic oxide of iron gives rise to the formation of ferric oxide and graphite. The nature of the reaction is, however, still under investigation.

In estimating the carbon of graphite it is advantageous to weigh the

carbonic acid produced by its combustion, as the loss on ignition is almost always greater than the amount of carbon present.

T. B.

Arsenic-glance.

By A. Frenzel (Jahrbuch f. Mineralogie, 1873, 25).

This name has been given to two minerals from the Palm-tree mine at Marienberg in Saxony, one of which, distinguished by brilliant metallic lustre and perfect monotomic cleavage, was found by Kersten to contain 97 p. c. arsenic and 3 p. c. bismuth, while the other, which occurs in irregular plates and nodules, appears to be merely impure metallic arsenic, its analysis giving—

As.	Sb.	Fe.	Ni.	S.	
92·80	2·28	1·60	0·26	1·06	= 98·00

Both varieties when set on fire continue to burn with a glimmering light. This property was shown by v. Kobell to belong to all varieties of finely divided arsenic, whence he inferred that arsenic-glance is not a distinct mineral species. It is most probable, however, that the first-mentioned mineral is really a distinct species, as its specific gravity, 5·3, is lower than that of either of its constituents, viz., arsenic 5·7, and bismuth 9·7.

H. W.

Copper Arsenide. By A. Frenzel

(Jahrbuch für Mineralogie, 1873, 26); also by A. Weisbach (*ibid.*, 64).

Frenzel has examined three varieties of this compound, regarded by mineral dealers as distinct species, and named accordingly. I. Domeykite from the San Antonio mine near Copiapo, Chile. II. Algodonite from Lake Superior. III. Whitneyite from Cerro las Paracutas, Cigazuala, Mexico. Analysis showed that all three are varieties of one species, Domeykite, viz.:—

	I.	II.	III.
Sp. gr. (at 22°) ..	6·700	7·207	7·547
Copper	70·16	72·02	72·99
Arsenic..........	25·89	28·29	27·10
Iron .... } Manganese .... }	3·50	—	—
Sulphur..........	0·49	—	—
Residue..........	0·45	—	—
	100·49	100·31	100·09

The formula of Domeykite, Cu^3As, requires 71·72 p. c. copper and 28·28 arsenic. The 25·88 p. c. of arsenic found in I would require, according to this formula, 65·66 p. c. copper. The copper arsenide in it is probably mixed with native copper, iron arsenide, and a sulphur compound. The third variety also probably contains native copper.

All three varieties exhibit, on newly fractured surfaces, a tin-white to silver-white colour. The bright metallically lustrous powder of II (the purest variety) is light grey; that of III dark grey; of I greyish black. In the course of 24 hours they all acquire a yellow tarnish.

Accompanying these minerals were found native copper, red copper ore, malachite, quartz, and small quantities of a radio-fibrous mineral, probably wavellite.

Weisbach describes a variety of Domeykite found imbedded in the argillaceous porphyry (*Thonsteinporphyr*) on the right bank of the Mulde, near Zwickau. It occurs in masses having a dense or very fine-grained fracture, with a decided tendency to cleavage, and therefore to crystalline structure. Colour and streak blackish grey. Lustre metallic, brighter on the streak. Hardness 5 (equal to that of apatite). Sp. gr., 6·84. Brittle, with decided inclination to softness. It differs from the Chilian mineral chiefly in colour and hardness, the latter being tin-white, and intermediate in hardness between calcspar and fluor-spar. This Zwickau mineral affords the first instance of the occurrence of Domeykite on the continent of Europe.

H. W.

Analysis of Copper-glance from Catamarca. By L. Schinnerer (Jahrbuch für Mineralogie, 1872, 977).

This massive copper-glance, of sp. gr. 4·7, showed distinctly iron pyrites and quartz crystals imbedded, and contained in 100 parts—

Cu.	S.	Fe.	As.	Zn.	SiO_2 (matrix).	Bi, Sb.	
48·82	26·71	6·64	9·16	0·74	7·52	traces	= 99·59

H. W.

Occurrence of Cuban in Sweden. By P. T. Cleve (Jahrbuch für Mineralogie, 1873, 90).

This mineral, first obtained from Cuba and examined by Breithaupt, has lately been discovered in two Swedish mines, namely those of Tunaberg and Kafveltorp. Three analyses agreed with the recognised formula, $\left.\begin{matrix}2FeS\\CuS\end{matrix}\right\}Fe_2S_3$.

H. W.

Beraunite. By A. Frenzel (Jahrbuch f. Mineralogie, 1873, 23).

This mineral, hitherto known only as a pseudomorph after vivianite, from the Hrbek iron mine at St. Benigna in Bohemia, has lately been found implanted on brown hæmatite, in the Father Abraham mine at Scheibenberg in Saxony. It forms laminar and radiate groups, also separate laminæ and rods running out in crystalline points, which indicate the form of gypsum. Colour hyacinth-red to reddish-brown; lustre nacreous to silky; streak-powder yellow. Sp. gr. 2·983. Analysis gave 54·50 Fe_2O_3, 28·65 P_2O_5, and 16·55 water, agreeing nearly with the formula $5Fe_2O_3.3P_2O_5 + 14H_2O$.

The pulverised mineral gives off only a little hygroscopic water at 100°, but when heated nearly to the boiling point of mercury, it gives off 13 20 p.c. water of hydration; and when strongly ignited, 3·35 p.c. more, which may be regarded as basic water: hence the mineral may be represented by the formula—

$$. 3Fe_2O_3 . P_2O_5 + 2Fe_2O_3 . 3H_2O . 2P_2O_5 + 11aq.$$

H. W.

Characters of the Mineral Species, Rittingerite. By A. Schrauf (Jahrbuch für Mineralogie, 1873, 92).

This name was given by Zippe to a mineral found in 1851, in the Joachimsthal, in small crystals, associated with red silver-ore, silver-glance, and galena. It was found to contain silver, sulphur, and arsenic, and the crystalline form, which exhibited a large number of faces, was recognised by Schabus as monoclinic, with the predominant faces ∞P and 0P. A few years ago Rittingerite came to light again, but under different circumstances, namely, in the form of separate crystals firmly imbedded in silver-pyrites. The specific gravity of these crystals was found by Schrauf to be 5·63; they contained 57·7 p.c. silver, together with arsenic and selenium. From the large proportion of silver and the occurrence of the prism of nearly 120°, Schrauf infers that the mineral belongs to the group of stephanite and polybasite. The crystals, which have numerous faces, are of tabular character from predominance of the base; subordinate are several hemipyramids, and the prism ∞P = 124° 30′. Twins occur very frequently, the individual crystals being joined either by a face 0P, or by the orthopinacoïd.

H. W.

Analyses of Syngenite from Kalusz in Gallicia, and Identity of Kaluszite with Syngenite. By Vrbal (Jahrbuch für Mineralogie, 1873, 88).

A comparison of the analysis of syngenite by Völker (v), (p. 254 of this volume), with those by Ullik, quoted by Rumpf in his description of kaluszite (i—iv):—

	I.	II.	III.	IV.	V.
Lime	17·14	17·09	16·76	16 62	16·97
Magnesia	—	—	—	—	0·46
Potassium oxide	28·57	28·53	28·40	28·72	28·03
Sulphuric anhydride	—	48·63	48·33	48·35	49·04
Water	5·50	5·46	5·46	5·45	5·81

shows that the whole may be represented by the formula $CaSO_4.K_2SO_4 + H_2O$, which requires 17 06 CaO, 28·70 K_2O, 48·75 SO_3, and 5·48 H_2O.

Rumpf regarded the mineral which he examined as monoclinic, and as Miller's measurement of artificial crystals having the same composition, indicated a rhombic form, Rumpf supposed that this potassio-calcic sulphate was dimorphous, and named the crystals which he

examined *kaluszite*, from the locality where they were found. Zepharowich, on the other hand, from the optical characters of syngenite, inferred that it belonged to the rhombic system; observing, however, that, without examination with the polarising apparatus, the crystals of syngenite, from their constant external character, might be regarded as monoclinic. Tschermak also found the crystals of "kaluszite" to be rhombic, the plane of the optic axes being parallel to 0P, and the apparent angle of the optic axes = 41° 36′ for red, and 49° 45′ for blue light. These facts leave no doubt as to the identity of kaluszite with the previously described syngenite, and therefore the name "kaluszite" may be dropped.

H. W.

Occurrence of Aluminite near Halle. By H. LASPEYRES (Jahrbuch f. Mineralogie, 1872, 951).

THIS mineral occurs in many localities, near Halle, in white, or more rarely yellowish crystalline nodules of various shape and size (up to that of the fist), also in strings and plates attached together, between strata and in clefts of the so-called Magdeburg sand. Where this carbonaceous and somewhat pyritiferous sand comes to the surface, and therefore in contact with the air, there is formed, by the mutual action of the atmospheric gases, the finely divided iron pyrites, and the fine particles of lignite and clay (kaolin particles and mica), a hydrated basic aluminium sulphate, namely aluminite. In these sands, which may be called "aluminite sands," the aluminite occurs so abundantly, where the conditions are favourable to its formation, that its nodules almost displace the sand.

H. W.

Miloschin. By A. KENNGOTT (Jahrbuch f. Mineralogie, 1872, 951).

AN analysis of a specimen of this mineral, which had been microscopically examined by Kenngott, and shown to be a mixture of an amorphous substance with numerous crystalline particles, was found by Marco Lecco, of Belgrade, to contain, when dried at 100°, 38·71 p.c. SiO_2, 43·45 Al_2O_3, 0·17 Cr_2O_3, and 8·47 water, agreeing approximately with the formula, $3SiO_2.2Al_2O_3 + 4H_2O$. The analytical numbers differ considerably from those formerly obtained by Kersten (*Pogg. Ann.*, xlvii, 485), viz., 27·50 p.c. SiO_2, 45·01 Al_2O_3, 3·61 Cr_2O_3, and 23·30 water, the difference doubtless arising from the mixed constitution of the mineral, as shown by the microscopical examination. It is better, therefore, not to regard the mineral as a simple aluminium silicate, represented by the formula $3SiO_2.2Al_2O_3 + 4H_2O$, but rather to conclude, from the resemblance of the crystalline particles to many specimens of kaolin when examined by the microscope, that it consists of kaolin ($H_2O.Al_2O_3 + H_2O.2SiO_2$) imbedded in an amorphous substance having the composition $H_2O.Al_2O_3 + H_2O.SiO_2$. This view represents the mineral as allied to the species called carolathin.

H. W.

Ardennite, a new Mineral containing Vanadium. By A. v. LASAULX (Jahrbuch f. Mineralogie, 1872, 930; 1873, 124).

THIS mineral occurs near Ottreg in the Belgian Ardennes mostly in thick-fibred cauliflower groups without recognisable crystalline forms, but exhibiting two directions of distinct cleavage. Small, well-defined crystals are also found, which, according to measurements by vom Rath, belong to the rhombic system, being derived from a rhombic octohedron in which the axial ratio is—

Brachydiagonal.		Macrodiagonal.		Principal axis.
0·4663	:	1	:	0·3135

Observed faces: $P \,.\, \bar{P}\frac{3}{2} \,.\, \infty P \,.\, \infty\bar{P}\frac{3}{2} \,.\, \infty\breve{P}_2 \,.\, \bar{P}\infty \,.\, \infty\bar{P}\infty \,.\, \infty\breve{P}\infty$. Cleavage perfect parallel to $\infty\breve{P}\infty$, distinct parallel to ∞P.

The colour of the mineral is colophony-brown, often also of a somewhat lighter yellowish colour; translucent with reddish colour in thin splinters; lustre waxy. Sp. gr. = 3·620. Melts before the blowpipe to a black glass, and gives a manganese bead with borax.

Quantitative analysis gave the following numbers:—

SiO_2.	Al_2O_3.	Fe_2O_3.	MnO.	CaO.	MgO.	V_2O_5.	Cu + P_2O_5.	H^2O.	
29·74	23·50	1·94	25·96	2·04	3·42	9·10	trace	4·04	= 99·74

agreeing nearly with the formula—

$$5(R_2O_3 \,.\, SiO_2 \,.\, RO \,.\, SiO_2) + 3RO \,.\, V_2O_5 + 5aq.$$

The water in ardennite is very intimately combined, and can be expelled only by strong and prolonged ignition.

In this respect, and likewise in its crystalline form, ardennite exhibits a considerable resemblance to ilvaite. The quantities of silica and alumina (or its equivalent in ferric oxide) also agree very nearly; but the quantities of manganous oxide, or its equivalent in ferrous oxide, differ considerably in the two minerals. Moreover ilvaite does not contain vanadium.

Ardennite occurs on a quartz vein of the crystalline slate near Ottreg, associated with smoke-grey quartz which is traversed by pyrolusite, violet and black compounds of manganese and iron, and crystalline aggregates of albite. None of these minerals contain a trace of vanadium, which element is, therefore, an essential constituent of ardennite.

The mineral called *dewalquite* from Salm-Chateau in Belgium, lately analysed by Pisani (p. 355 of this volume), is evidently the same as ardennite, although the amount of vanadic acid found by Pisani is much less than that found by v. Lasaulx.

H. W.

Staurolite. By A. v. LASAULX (Jahrbuch f. Mineralogie, 1872, 946).

THE great diversities of composition exhibited by specimens of this mineral from different localities have been shown by v. Lasaulx to be due, as first suggested by Lechartier, to microscopic admixtures of

other minerals. Thin sections of the large red-brown crystals of staurolite from the mica-slate of Sterzing in the Tyrol, were found by microscopic examination to be interspersed with crystals of garnet and quartz, the quartz itself, moreover, enclosing scales of mica and pores filled with liquid, and the garnet enclosing magnetic iron ore, brookite, and quartz. The same minerals were found imbedded in staurolite from Pfitsch. Staurolite from Morbihan, in Bretagne has a finely cellular structure, all the pores being filled with quartz. A similar structure is exhibited by that of Aberdeenshire, which also contains brookite, magnetic iron ore, and mica. Black staurolite from Winkelsdorff in Moravia is traversed by fine parallel veins of quartz and brown mica. Fine red-brown crystals from Faido exhibit scarcely any traces of enclosed minerals, whereas others from the paragonite slate of Airolo exhibit the most various transitions, from such as are quite free from enclosed minerals to such as are quite filled with them.

It is evident, then, that the true chemical composition of staurolite can be determined only from specimens which are shown by the microscope to be free from enclosed minerals. Such a specimen from Monte Campione (sp. gr. 3·71) gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	H_2O.	
29·81	48·26	5·31	12·03	3·25	0·86	= 99·52

leading to the formula—

$$2\left.\begin{matrix}(Fe\,;\ Mg)''\\(Al_2\,;\ Fe_2)^{vi}\\2Si^{iv}\end{matrix}\right\}O_{11},\ \text{or}\ (Fe\,;\ Mg)''O\ .\ 2Al^2O^3\ .\ 2SiO^2.$$

If now it be admitted that alumina and ferric oxide, also magnesia and ferrous oxide, replace one another, and that variations in the amount of iron may be explained by admixtures of magnetic iron ore and garnet; in that of magnesia by admixture of biotite; and in that of alumina by admixture of cyanite: the analyses with higher amount of silica, if re-calculated in accordance with the amount given by the above formula, will agree tolerably well with that formula, small differences being due to the admixtures above mentioned. For it must be remembered that the microscope shows that, of all the minerals imbedded in staurolite, quartz is by far the most abundant.

H. W.

Conversion of Garnet into Chlorite. By J. NIEDZWIEDKI (Jahrbuch f. Mineralogie, 1872, 951).

PSEUDOMORPHS of chlorite after garnet have often been observed. The one here noticed, from the Saualp in Corinthia, exhibits the half of a garnet-dodecahedron broken through the middle and surrounded by a crust of chlorite about 4 mm. thick. The garnet has a colombo-red colour and fatty lustre; the chlorite is dark-green with fine scaly structure. The thin laminæ of chlorite appear to be deposited on the faces of the crystal very irregularly, and the surface of separation of the garnet and chlorite is irregularly zig-zagged. Under the microscope it is plainly seen that the chlorite has been formed from the garnet.

Analysis of the two minerals gave—

SiO_3.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	H^2O.	
38·59	17·57	16·43	21·12	2·27	4·27	—	= 100·25
25·19	21·66	9·09	14·92	—	18·73	11·53	= 100·42

To convert the garnet into chlorite a third of the silica (13 p. c.), a third of the ferric oxide, a third of the ferrous oxide, and the whole of the lime have been removed, and at the same time 14 p. c. of magnesia and 11 p. c. water have been added.

H. W.

Analysis of Gabbro from Prato in Tuscany. By E. DRECHSLER (Jahrbuch f. Mineralogie, 1872, 977).

THE specimen examined is from the boundary between the gabbro and serpentine, and contains particles of serpentine, together with plagioclase and diallage. The mixture is coarse-grained, and has a specific gravity of 2·849. Analysis gave :—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	CaO.	MgO.	K_2O.	Na_2O.	H_2O.
55·58	18·58	5·49	1·29	12·05	1·08	0·42	3·09	2·01=99·59

H. W.

On the Cause of the Tumefaction of Obsidian Exposed to a High Temperature. By MM. BOUSSINGAULT and DAMOUR (Compt. rend., lxxvi, 1158—1165).

HUMBOLDT, among others, has noticed the tumefaction of obsidian when it is exposed to a white heat; he attributed it to the evolution of gas when the mass is of a pasty consistence, and in conjunction with Rose and Karsten, he endeavoured, but without success, to collect and measure the gas evolved. Spallanzani (*Voyage dans les Deux Siciles*, vol. iii, 232) also failed in collecting the gas, and attributed the swelling up to the volatilization of the more easily fusible silicates. He obtained, however, in the distillate a small quantity of water acidified with hydrochloric acid.

Obsidian is a felspathic rock, the only volatile constituents being water and chlorine. The authors have repeated Humboldt's experiments, with the view of determining the presence of these two substances in the volatilised portion. They directed their attention especially to the solution of the following questions:—What is the loss suffered by obsidian on heating? Is gas evolved during ignition? What amount of water and hydrochloric acid is given off? Does obsidian lose chlorine by ignition? Between four and five grams of the mineral were heated to an orange-red heat, at which temperature it swelled up; it finally melted at a white heat. Different specimens lost from 0·104 per cent. to 0·73 per cent. It increases from two to seven times its original volume; at a dull red, or even at a cherry-red heat it undergoes no change and suffers no loss. To solve the second question, a quantity was heated to whiteness in a porcelain retort previously exhausted by means of a Sprengel's air-pump; 117 grams of the substance gave on the average 10—12 cm. of a gas which

proved to be a mixture of nitrogen and carbonic anhydride. This quantity is far too small to account for the extraordinary increase in bulk. A distillate was, however, obtained which on investigation proved to be solution of *pure* hydrochloric acid in water; a quantity of chlorides was, besides, deposited at the neck of the retort. The sum of the water and the chlorine agreed pretty well with the loss on heating the mineral. The hydrochloric acid is given off presumably by the action of water-vapour on chlorides at a high temperature, for it is not evolved till the temperature has reached 800°, when its tension must be considerable; the mass is in a pasty state, and the water and hydrochloric acid escaping suddenly in the form of vapour, produce the peculiar phenomenon. If obsidian be reduced to a fine powder and dried before ignition, no tumefaction occurs.

W. R.

Crystallography.—Development of the Chief Propositions in Crystallography and Crystalline Physics. By A. Brezina (Jahrbuch f. Mineralogie, 1873, 83).

On Perowskite from Wildkreuzjoch, Pfitschthal. By F. Hessenberg (*ibid.*, 77).

The Twin-laws of Anorthite. By G. vom Rath (*ibid.*, 78).

On Fahl-ore and its regular Twin-formations. By A. Sadebeck (*ibid.*, 80).

Calcspar from the Rödefjord, Iceland. By F. Hessenberg (*ibid.*, 87).

Aragonite from Sasbach. By A. Schrauf (*ibid.*, 89).

Quartz-crystals from the Wallis. By Weiss (*ibid.*, 90).

A Pseudomorph of Dolomite after Garnet. By G. Laube (*ibid.*, 91).

On the Composition and Origin of the Waters of a Salt Spring in Huel Seaton Mine. By J. A. Phillips (Chem. News, xxvii, 62).

Huel Seaton Copper Mine is situated about one mile north-east of the town of Camborne in Cornwall, and about three miles from the sea. The workings of the mine are entirely in "killas" or clay-slate, and the saline waters issue at the rate of 50 gallons per minute, and at a temperature of 92° F., from the eastern fore-breast of the 160-fathom level. This has intersected a fault, or cross-course, which may be traced in a northerly direction to the sea. The temperature of the level from the end of which the water issues, like that of the water itself, is 92° F. The following results in grams per litre and grains per gallon were obtained by analysis. Specific gravity 1·0123. Total solid contents 14·3658 grams per litre, or 1005·61 grains per gallon.

	Grains per litre.		Grains per gallon.	
	I.	II.	I.	II.
Carbonic acid	0·0795	0·0786	5·56	5·50
Sulphuric acid	0·0178	0·0177	1·25	1·24
Silica	0·0270	0·0280	1·89	1·96
Chlorine	9·1728	9·1662	642·10	641·63
Bromine	trace	trace	trace	trace
Alumina	0·3456	0·3460	24·19	24·22
Ferric oxide	0·0031	0·0033	0·22	0·23
Manganese	trace	trace	trace	trace
Copper	minute trace	minute trace	minute trace	minute trace
Lime	3·4795	3·4963	243·56	244·74
Magnesia	0·0721	0·0710	5·05	4·97
Alkaline chlorides	6·4920	6·4626	454·44	452·38
Potassium	0·0832	0·0835	5·82	5·84
Cæsium	trace	trace	trace	trace
Sodium	2·2977	2·2885	160·84	160·19
Lithium	0·0805	0·0794	5·63	5·56
Ammonia	trace	trace	trace	trace
Nitric acid	trace	trace	trace	trace

The foregoing results may be thus tabulated:—

	Grains per litre.		Grains per gallon.	
	I.	II.	I.	II.
Calcium carbonate	0·0921	0·1011	6·45	7·08
Ferrous carbonate	0·0045	0·0047	0·31	0·33
Manganous carbonate	trace	trace	trace	trace
Cupric chloride	minute trace	minute trace	minute trace	minute trace
Calcium chloride	6·7697	6·7934	473·88	475·54
Magnesium chloride	0·1712	0·1686	11·98	11·80
Aluminium chloride	0·9003	0·9013	63·02	63·09
Potassium chloride	0·0919	0·0900	6·43	6·30
Cæsium chloride	trace	trace	trace	trace
Sodium chloride	5·8412	5·8210	409·00	407·47
Lithium chloride	0·4888	0·4820	34·22	33·74
Calcium sulphate	0·0303	0·0301	2·12	2·11
Potassium bromide	trace	trace	trace	trace
Potassium silicate	0·0693	0·0719	4·85	5·03
Nitric acid	trace	trace	trace	trace
Ammonia	trace	trace	trace	trace
Total found by addition of constituents	14·4623	14·4641	1012·35	1012·49
Total found directly	14·3658	—	1005·61	—
Free carbonic acid	0·0373	0·0323	2·61	2·26

The difference between the amount of solid constituents found directly, and that obtained by addition of constituents is doubtless in great measure due to the partial decomposition of aluminium and mag-

nesium chlorides at the temperature (180°) at which the drying of the residue was effected.

A consideration of the various phenomena connected with the occurrence of this and other apparently similar springs which have at different times been discovered in the same district, would seem to lead to the inference that they all have some more or less direct communication with the sea, and that they are either the result of infiltration of sea-water through faults, or are true and independent sources which, being tapped below the sea level, had found their way to the ocean through faults or channels.

The following is a not improbable explanation of the origin of the spring. The cross-course is believed to extend through both granite and clay-slate to the sea. From the close contact of its surfaces, the presence of clay, and from other causes, this fault may be supposed not to be uniformly permeable by water, which can only follow a circuitous passage. In this way it penetrates to depths where reactions take place, which, although not entirely in accordance with the results of daily experience in our laboratories, can, after the investigations of Daubrée, Sénarmont, and others, be readily understood. By the action of sea-water on calcium silicates, sodium silicates and calcium chloride may be produced. The sodium sulphate of the sea-water will be decomposed by this calcium chloride, with production of calcium sulphate and sodium chloride. The decomposition of clayey matter by common salt may produce aluminium chloride and sodium silicates, while the magnesium of the magnesium chloride may be replaced by calcium; lastly a portion of the potassium in the sea-water appears to have been replaced by the lithium of the granite.

J. B.

Mineral Waters of Vichy and its Neighbourhood.

By De Gouvenain (Compt. rend., lxxvi, 1063—1066).

The presence of iodine and bromine in these waters having been asserted by some chemists and denied by others, the author examined the mother-liquors which are left on evaporating the waters for the purpose of obtaining the salts dissolved. In the Vichy water proper, after such concentration, he found abundant evidence of the presence of iodine and bromine. The mother-liquor from the Grand-Grille water contained bromine equivalent to ·0008 gram per litre of the original water, but only a trace of iodine. The Vichy mother-liquor contained 0·583 per litre of fluorine. The Grand-Grille water contained 0·0076 fluorine per litre. In the mother-liquors of these waters, the author found, also, boron, arsenic, lead, copper, rubidium, cæsium, and nitric acid. The calcareous deposit at the Grand-Grille contained arsenic, lead, copper, cobalt, zinc, aluminium, and manganese. No fluorine was found, probably because it exists in the water as a soluble alkaline fluoride. At the same source there is also found a mud which consists chiefly of ferric arsenate. The same substances are met with in the deposit at the Vaisse spring, where there is no metallic conduit from which they might have been derived. The calcareous deposit at the Hôpital spring contains much arsenic and traces of copper. In the

radiating arragonite which forms the rock of the Celestins were found lead, copper, and phosphoric acid. The Bourbon-l'Archambault water contains only a trace of iodine, 0·00684 gram of bromine, 0·00268 gram of fluorine per litre, and traces of cæsium and rubidium. The calcareous deposits in the same locality contain iron, manganese, magnesium, and strontium. The sides of the principal reservoir are also coated with a brown mud containing manganese and arsenic. The Néris water contains bromine, traces of iodine, and 0·00614 gram of fluorine per litre.

B. J. G.

Gases contained in Sea-water. By O. JACOBSEN (Ann. Chem. Pharm., clxvii, 1—38).

THE author was on board the "Pomerania" in her expeditions to the East and North Seas during the last two years.

For the methods used in collecting the water, expelling and collecting the gases, &c., reference must be made to the original paper; the apparatus is similar to that used in the "Challenger."

The amounts of oxygen and nitrogen in surface-water were found to be almost constant, the mean of 24 samples giving 33·93 per cent. O and 66·07 per cent. N (if O + N = 100). In deep water the amount of oxygen is very little less, generally speaking, than in shallow waters, in places, however, where the deep water is very dense, and where it lies in an undisturbed state for a long time (as in bays) the amount of oxygen sinks greatly. In such localities the water also frequently smells of sulphuretted hydrogen.

The total amount of the gases in sea-water varies but very slightly with the depth. The author lays it down as a rule that the amount of oxygen and nitrogen in deep water is equal to that which water of the same temperature would absorb at the surface, minus a small quantity of oxygen which has been used in processes of oxidation.

By boiling sea-water only a small fraction of the carbon dioxide which it contains is expelled, and it is only by distilling the water in a current of air freed from carbon dioxide, that the whole of this gas can be got out of the water.

There exists a proportion between the quantity of saline constituents of the water and that of the carbon dioxide, but otherwise the amount of this gas does not appear to be influenced by the depth. Careful estimations were made of the quantities of earthy carbonates in various waters; these were found to vary from ·018 to ·028 gram per litre (calculated as $CaCO_3$) in the northern parts of the North Sea, to ·03 and ·0325 near the southern shores of the same sea. If all the carbonates are calculated to bicarbonates, there still remains an excess of carbon dioxide; this the author regards as important, because we learn that some of this gas exists in a state in which the expired breath of sea animals may be directly added to it, and in which it is also accessible to sea plants.

M. M. P. M.

The Influence of a Limited Supply of Air on the Sulphuretted Waters of Eaux-Bonnes. By L. MARTIN (Ann. Chim. Phys. [4], xxviii, 289—323).

EXPOSURE of the water drawn from the various springs of Eaux-Bonnes to a limited supply of air, leads to the complete conversion of the sodium monosulphide which is present, into sodium bisulphide; the soda thus set at liberty combining with the silicic acid contained in the water. As silicic acid is always present in the proportion of two equivalents for each equivalent of sulphur contained in the water, it follows that the sodium silicate formed should be a quadrisilicate. The same ratio between the sulphur and the silicic acid obtains also in the water of Saint Sauveur and in that of Cauterets, although in these cases the silicic acid is present as a silicate.

Further exposure of the water to the action of air causes the sodium bisulphide to be partially transformed into sodium thiosulphate, and when the recent water is heated to 80°—90°, in contact with a limited supply of air, the sodium bisulphide first formed is rapidly oxidised to bisulphate. If the water thus heated be mixed (as in the case of an ordinary bath), with 3 parts of the recent water, and the mixture be exposed to the air, the sulphur becomes entirely oxidised in the course of about 24 hours.

During the above changes no polysulphides of a higher degree than bisulphide are formed, and there is no loss of sulphur, it being found that the oxidised water contains the same proportion of this element as the recent water.

The sulphides and thiosulphates were estimated together by means of a titrated solution of iodine in potassium iodide, a slight excess of barium chloride having been previously added to decompose alkaline carbonates and silicates. Another sample of the water was then precipitated by zinc acetate, and the thiosulphates were estimated in the filtrate by means of the standard iodine solution.

T. B.

The Nature of the Sulphur Compound contained in the Thermal Waters of the Pyrenees; and the Changes which Alkaline Sulphides undergo on Dilution. By E. FILHOL (Ann. Chim. Phys. [4], xxviii, 529—533).

BÉCHAMP has contended that when a small quantity of water acts on the monosulphide of calcium or of magnesium, decomposition takes place, a metallic hydrate and sulphydrate being formed, and that a greater degree of dilution causes the reaction to proceed further, the whole of the base then taking the form of hydrate, and sulphydric acid being liberated. He also considers that alkaline sulphides undergo a similar decomposition when their solutions are largely diluted; and consequently many mineral waters which are supposed to contain sodium monosulphide should be regarded as containing sodium hydrate and sulphydric acid.

The author considers that this decomposition does not take place when a solution of sodium monosulphide is diluted, and he contends

that the fact of a solution of sodium monosulphide yielding calcium hydrate when it is mixed with a calcium salt, does not prove the existence of sodium hydrate in the solution of the monosulphide, the precipitation being due to the insolubility of the calcium hydrate. Similarly he considers that the formation of calcium hydrate by the action of water on calcium sulphide is brought about by the insolubility of the base. If this view be not accepted, a solution of sodium carbonate should be regarded as containing sodium hydrate and free carbonic acid, as it yields *magnesia alba* and not magnesium carbonate when it is added to a solution of a magnesium salt; but a dilute solution of sodium carbonate does not contain sodium hydrate and free carbonic acid, as boiling does not separate the latter and lead to the formation of caustic soda in the liquor.

In order to elucidate this question, the author prepared a solution of sulphydric acid containing about the same proportion of sulphur as the water of Eaux-Bonnes, and treated one portion of it with sufficient caustic soda to convert its sulphydric acid into sodium monosulphide, and another portion with sufficient soda to convert its sulphydric acid into sodium sulphydrate. These two solutions and a portion of the original solution were treated with a current of well-washed hydrogen, care being taken to make the conditions similar in each case, and it was found that the simple solution of sulphydric acid was always desulphurised long before those to which alkali had been added. It was also found that the solution to which sufficient soda had been added to produce monosulphide, resisted the action of the stream of hydrogen much longer than that to which only half the quantity had been added, and the smell of the former solution was considerably less intense than that of the latter. Although a long-continued current of hydrogen can remove the whole of the sulphur from a solution of sodium monosulphide, the author considers that the amount of monosulphide decomposed by the water is very limited, and that almost the whole of the sulphur exists as sodium monosulphide.

The waters of Bagnères-de-Luchon and Eaux-Bonnes were found to behave like a solution of sodium monosulphide when they were treated with a current of hydrogen.

When three solutions containing the same proportion of sulphur, existing as sulphydric acid, sodium sulphydrate, and sodium monosulphide respectively were exposed to the air, it was found that the first was decomposed several days before either of the others, and that the solution containing sodium sulphydrate was decomposed several days before that of sodium monosulphide. In the case of the solution of sulphydric acid, sulphur is deposited and no sulphuric acid is formed; but in the cases of the sodium sulphydrate and the sodium monosulphide, sodium sulphate is formed, more being produced in the latter case than in the former.

A dilute solution of sodium sulphydrate on exposure to the air, or on the addition of water containing dissolved oxygen, acquires a greenish-yellow colour, indicative of the formation of polysulphides. This phenomenon is not observed in the case of a solution of sodium monosulphide, but if water containing carbonic acid and oxygen be added, the monosulphide is converted into sulphydrate and the colora-

tion takes place. A similar effect may be produced by the addition of a small proportion of iodine and exposure to the air. These results remain unexplained if we assume that the monosulphide solution contains free sulphydric acid and sodium hydrate, but are readily comprehensible if sodium monosulphide be considered as existing in the solution.

Arsenious acid gives no precipitate with the sulphurous waters of the Pyrenees, although it produces a precipitate with waters containing free sulphydric acid, such as those of Enghien.

T. B.

The Sulphuretted Springs of S. Venera al Pozzo, at the Eastern Base of Etna. By O. SILVESTRI (Gazzetta chimica italiana, iii, 35).

THE water of the spring is colourless and very clear when freshly drawn, but on exposure to the air it acquires a greenish tint, becomes milky, and exhales the odour of hydrogen sulphide. Its specific gravity is 1·002836 at 19°.

The temperature of the water at the spring is nearly the same as that of the external air. By prolonged exposure to the air the water undergoes alteration, from the development of a green cryptogamous plant, the putrid fermentation of which gives rise to the evolution of miasmatic gases, including sulphydric acid, carbonic anhydride, and marsh-gas. The growth of this plant depends on the influence of light, air, and the gases dissolved in the water.

The composition of the water is as follows:—

		grams.
Weight of a litre at 19°		1000·26596
Gaseous matter evolved on boiling = 0·23450 gram consisting of ..	Sulphydric acid	0·01547
	Carbonic anhydride	0·18453
	Marsh-gas	0·00757
	Oxygen	0·00016
	Nitrogen	0·02677
Volatile matter separated by complete evaporation to dryness: 997·03164 grams consisting of	Pure water	997·03102
	Sal-ammoniac	0·00062
Total fixed matter or residue of saline substances dried at 100° = 3·600 grams, or dried at 180°		3·124
Part of the residue rendered insoluble in pure water by heat: neutral carbonates of calcium and magnesium, silica, phosphate and fluoride of calcium, oxide of manganese, organic matter		0·206
Part of the same residue consisting of soluble salts ..		2·918
Salts of calcium and magnesium, deduced from the degree of hardness		0·46
Total sulphydric acid		0·01517
Sulphydric acid combined as alkaline sulphide		0·00030
Total carbonic anhydride		0·51480
Carbonic anhydride given off on boiling		0·18453

		grams.
Carbonic anhydride of the neutral carbonates of calcium, magnesium, and strontium		0·05480
Total lime		0·07300
Lime remaining dissolved after boiling		0·00700
Lime of the neutral carbonate		0·06600
Total magnesia		0·00698
Magnesia remaining dissolved after boiling		0·00248
Magnesia of the neutral carbonate		0·00286
Sodium (calculated from the chloride)		1·07521
Potassium		0·00035
Lithium		0·00120
Ammonium		0·00021
Manganese		0·00020
Iron (trace).		
Sulphuric anhydride		0·01037
Chlorine		1·64809
Bromine (trace).		
Iodine		0·01250
Fluorine (trace).		
Silica		0·00050
Matter precipitable by ammonia: 0·00072 gram, consisting of	Aluminium phosphate	0·00050
	Manganese oxide	0·00012
	Calcium fluoride, Iron } traces.	
Organic matter		0·02880

The hardness of the water (determined by the hydrotimeter) is 46°, of which 2° are due to carbonic anhydride, 28° to calcium carbonate, 13·5° to other calcium salts, and 1·5° to the carbonate and other salts of magnesium.

H. W.

Organic Chemistry.

Influence of Electricity on Mixtures of (*a*) Marsh-gas and Carbon Dioxide, (*b*) Hydrogen and Carbon Monoxide. By P. Thénard and A. Thénard (Compt. rend., lxxvi, 1049—51).

The authors had been making experiments similar to those described by Sir B. Brodie (p. 744 of this volume) before his paper was published. It now appears that they had gone a step further than that chemist. He found the contraction of a mixture of hydrogen and carbon dioxide under the influence of electricity, so sluggish after five hours that he considered the experiment to be practically completed. The authors had, however, found that the contraction went on till the product was liquid. (Sir B. Brodie mentions indeed a liquid of similar properties as being formed by the contraction of a mixture of marsh-gas and carbon dioxide, but he does not appear to have observed any liquid when working with hydrogen and carbon monoxide, though he

says marsh-gas and carbon dioxide were formed under these conditions). The gaseous mixtures used by the authors were (*a*) marsh-gas and carbon dioxide, (*b*) hydrogen and carbon monoxide. The liquids obtained in each case were colourless and oily at first, but soon became amber-coloured and resinous. The liquid from (*a*) became brown when heated to 100°. It was slightly soluble in water, giving a yellow, opalescent, very acid solution, having an odour of metacetone (? propione) mixed with formic compounds. It reduced mercuric oxide and behaved like sugar or tartaric acid when it was ignited. On treatment with potash it formed a salt whose acid was precipitated by hydrochloric acid and was soluble in excess. The mixture (*b*) gave a liquid somewhat less resinous than the preceding, but of a similar odour, very soluble in water, yielding a brandy-yellow solution, very acid, and slightly opalescent. It behaves like the other compound when ignited. It reduced Fehling's solution, silver nitrate, mercuric chloride, and oxide. It was not fermentable. When half neutralised with potash, and taken up with a mixture of alcohol and ether, it presented the appearance of beer-yeast. Berthelot considers that these liquids result from the condensation of formic aldehyde, CH_2O, which, he considers, would be the first product of the reaction between hydrogen and carbon monoxide. The authors draw attention to the fact that acetic acid is broken up under the influence of electricity, carbon dioxide, or else marsh-gas, being given off, and a brown residue soluble in potash being left. They think that this decomposition throws some light on the changes which took place in their experiments.

B. J. G.

Action of Ozone on Alcohol, and the Combination of Cyanogen with Hydrogen under the Influence of the Silent Electric Discharge. By A. Boillot (Compt. rend., lxxvi, 1132).

When anhydrous alcohol is treated with ozonised air or ozonised oxygen, an action takes place resulting in the formation of acetic acid and formic acid, acetic ether being apparently produced at the same time; and when the product of the reaction is allowed to evaporate spontaneously, a white powder, soluble in alcohol and water, is deposited. This substance is still under examination.

When a mixture of cyanogen and hydrogen is exposed to the action of the silent electric discharge, other products besides hydrocyanic acid are formed, which, however, have not yet been examined.

T. B.

Conversion of Bromoform into Carbon Tetrabromide. By J. Habermann (Deut. Chem. Ges. Ber., vi, 174—175).

This reaction readily takes place when a mixture of bromoform, bromine, and dilute potash is exposed to direct sunshine for 5—6 days—

$$CHBr_3 + Br_2 + KOH = CBr_4 + KBr + H_2O.$$

If no potash be present the reaction goes on much more slowly.

C. S.

The Action of some Chlorides on Sodium Ethylate. By A. GEUTHER and F. BROCKHOFF (Jenaische Zeitschrift, vii, 359—373).

Phosphorus Pentachloride and Sodium Ethylate.—When these substances were made to act on one another in the proportion indicated by the subjoined equation, the products indicated were obtained, together with some alcohol and a small quantity of an ethyl phosphate which yielded phosphoric acid on fusion with sodium carbonate and sodium nitrate:—

$$PCl_5 + 4C_2H_5ONa = 4NaCl + C_2H_5Cl + PO(OC_2H_5)_3.$$

This reaction may be regarded as taking place in two stages, thus:

$$(1.)\ PCl_5 + C_2H_5ONa = POCl_3 + C_2H_5Cl + NaCl.$$
$$(2.)\ POCl_3 + 3C_2H_5ONa = PO(OC_2H_5)_3 + 3NaCl.$$

Perchlorethylene and Sodium Ethylate.—The action of sodium ethylate on perchlorethylene has been studied by Fischer and Geuther, who found that, besides sodium chloride, sodium ethylglyoxalate, and ethyl dichlor-acetate, there were also produced two substances having the composition $C_4H_5Cl_3O$ and $C_8H_{16}Cl_2O_3$. These substances have since been proved to be trichlorethoxyl-ethylene and tri-basic ethyl dichloracetate. The authors consider trichlorethoxyl-ethylene to be the primary product of the reaction, being derived from perchlorethylene by the replacement of one atom of chlorine by one atom of ethoxyl:—

$$C\genfrac{}{}{0pt}{}{CCl_2}{Cl_2} + C_2H_5ONa = C\genfrac{}{}{0pt}{}{CCl_2}{Cl(OC_2H_5)} + NaCl.$$

The tribasic ethyl dichloracetate may be derived from the above compound as follows, the sodium ethylate originally employed having contained alcohol:—

$$(1.)\ C\genfrac{}{}{0pt}{}{CCl_2}{Cl(OC_2H_5)} + C_2H_5ONa = C\genfrac{}{}{0pt}{}{CCl_2}{(OC_2H_5)_2} + NaCl.$$

$$(2.)\ C\genfrac{}{}{0pt}{}{CCl_2}{(OC_2H_5)_2} + C_2H_5OH = C\genfrac{}{}{0pt}{}{CHCl_2}{O(C_2H_5)_3}.$$

The ethyl dichloracetate may arise from the action of water on tribasic ethyl dichloracetate, the water being partly hygroscopic and partly derived from secondary reactions:—

$$C\genfrac{}{}{0pt}{}{CHCl_2}{(OC_2H_5)_3} + H_2O = \begin{array}{c} CHCl_2 \\ | \\ CO \\ | \\ OC_2H_5 \end{array} + C_2H_5OH.$$

The action of sodium ethylate on this ether gives rise to ethyl diethylglyoxalate, this compound being subsequently decomposed by sodium hydrate into alcohol and sodium diethyl glyoxalate:—

$$(1.)\quad \begin{matrix} CHCl_2 \\ CO \\ OC_2H_5 \end{matrix} + 2C_2H_5ONa = \begin{matrix} CH(OC_2H_5)_2. \\ CO \\ OC_2H_5 \end{matrix} + 2NaCl.$$

$$(2.)\quad \begin{matrix} CH(OC_2H_5)_2 \\ CO \\ OC_2H_5 \end{matrix} + Na = \begin{matrix} CH(OC_2H_5)_2 \\ CO \\ ONa. \end{matrix} + C_2H_5OH.$$

The above-mentioned intermediate reactions were confirmed by experiments in which the action of the sodium ethylate was to some extent limited.

The action of sodium ethylate free from alcohol on perchlorethylene, gave rise to the products enumerated above, but in smaller quantities, also to a gas burning with a blue flame, and some brown products.

Perchlorethane and Sodium Ethylate.—When an ethereal solution of perchlor-ethane was heated to 106°—110° with sodium ethylate, an energetic action took place, a gas burning with a non-luminous flame being evolved. The products of the reaction were distilled, and perchlorethylene was found in the distillate, accompanied, as might be expected, by those substances which are formed by the action of sodium ethylate on it. Besides sodium chloride and resinous substances, the residue contained sodium ethyl-glyoxalate and sodium acetate. The author considers that the latter is formed by the oxidising action of chlorine on sodium ethylate, the chlorine being yielded by the perchlorethane.

$$3C_2H_5ONa + 2Cl = C_2H_3NaO_2 + C_2H_6 + C_2H_6O + 2NaCl.$$

The portion of the resinous products which dissolved in soda gave, after treatment with hydrochloric acid, 66·5 to 67·7 per cent. of carbon and 5·5 to 6·1 per cent. of hydrogen, and the portion which was insoluble, gave 67·1 per cent. of carbon and 4·7 per cent. of hydrogen.

Trichlorethylene Chloride and Sodium Ethylate.—These substances react readily on one another, perchlor-ethylene being produced. Similar results were obtained when the trichlorethylene chloride was dissolved in ether and then treated with sodium ethylate.

Dichlorethylene Chloride and Sodium Ethylate.—Dichlorethylene chloride was digested for some time with sufficient alcoholic sodium ethylate to replace all the chlorine by ethoxyl. The product was then distilled, and by the addition of water to the distillate, an oil was obtained which possessed the composition of—

Dichlorethoxyl-ethylene.—This substance is a colourless liquid having a peculiar aromatic odour. It boils at 128·2 (cor.), and has a specific gravity of 1·08 at 10°. Moisture acts slowly on it, hydrochloric acid and ethyl chloride being formed. Heated in a sealed tube to 180° with excess of water, it is entirely decomposed with formation of glycollic acid, hydrochloric acid, and ethyl chloride:

$$C\begin{matrix} CHCl \\ Cl.OC_2H_5 \end{matrix} + 2H_2O = \begin{matrix} CH_2OH \\ CO \\ OH \end{matrix} + ClH + C_2H_5Cl.$$

Excess of alcoholic sodium ethylate converts dichlor-ethoxyl ethylene into the sodium salt of ethyl-glycollic acid, and the author considers it probable that ethyl monochloracetate is formed as an intermediate product. A small quantity of the latter was apparently formed during the action of sodium ethylate on dichlorethylene chloride, and it may be also formed, together with ethyl chloride, by the action of sodium ethylate on excess of dichlor-ethoxyl-ethylene.

Monochlorethylene Chloride and Sodium Ethylate.—When monochlor-ethylene chloride is treated with excess of sodium ethylate, an action takes place resulting in the formation of dichlorethylene and a small quantity of sodium acetate. The action of sodium ethylate on dichlorethylene is under investigation.

Perchloromethane and Sodium Ethylate.—One molecule of carbon tetrachloride was diluted with two volumes of ether and treated with 4 molecules of sodium ethylate, the whole being then digested for about 4 hours under a slightly increased pressure. After the reaction, during which no gas was evolved, had terminated, the product was distilled and the distillate was found to contain no portion boiling above 75°. The residue in the retort contained a brown substance insoluble in water which, after washing with hydrochloric acid, contained 63·6 per cent. of carbon and 72 per cent. of hydrogen. This substance contained no chlorine and yielded no ash.

The alkaline liquor obtained by heating the residue with water yielded, when treated with hydrochloric acid, a brown resinous precipitate, soluble in alkalies and alcohol. It contained 60·8 per cent. C., and 6·2 per cent. H. The alkaline liquor also contained traces of carbonic acid and oxalic acid.

T. B.

Action of Sodium Sulphide upon Glycerin.

By F. Schlagdenhauffen (Compt. rend., lxxvi, 1021—23).

Crystallised sodium monosulphide was heated in a retort with half its weight of glycerin for 20 hours. At the expiration of this time an oily liquid began to distil, and the operation was continued until the contents of the retort became dry.

On rectification, the first portions of the distillate passed over between 50° and 70°, but the boiling point rose continuously to 200°. By fractionating the portions of low boiling point, a liquid was finally obtained, which boiled regularly at 58°; its density was 0·825, and it possessed an odour resembling that of mercaptan. From this latter circumstance, the author supposed that it might prove to be *ethyl* sulphydrate, but the analytical numbers were far from supporting such a conclusion. The liquid dissolved mercuric oxide, and when saturated separated into two layers, the lower of which solidified into a crystalline mass. The crystals were soluble in ether, carbon sulphide, and alcohol, and separated well from the latter solvent. Their melting point was 38°.

Potassium sulphocyanate appeared to act upon glycerin in a manner analogous to that of sodium sulphide. No further analyses seem to

have been made, and the investigation is left in the above unfinished state.

J. W.

Sulphovinic Acid and its Salts. By BERTHELOT (Bull. Soc. Chim. [2], xix, 295—300).

THE author gives the results of his experience in working with sulphovinic acid and its salts since his first memoir upon the subject was published.

I. *Action of Sulphuric Acid upon Alcohol.*—Different products are obtained according to the temperature of the mixture. (*a*). If the two substances are mixed in small quantities at a time, the temperature being kept at 0°, no reaction takes place at first. After prolonged contact, however, a sulphovinic acid is formed, the salts of which differ from those of the ordinary acid, into which they are changed by boiling. Svanberg (*Berzelius' Traité de Chimie*, vi, 586) first discovered this peculiar acid, the existence of which has been since confirmed by Gerhardt and the author, but denied by Erlenmeyer, who probably neglected the precautions which are necessary to prevent this acid from being transformed into the ordinary one. The presence of these unstable sulphovinates is, perhaps, one of the causes of the spontaneous decomposition of the sulphovinates found in commerce. (*b*.) When concentrated sulphuric acid and absolute alcohol are mixed without being cooled, the proportion of ethylsulphuric acid formed depends upon the degree of local heat, and the proportion of the two substances to each other. Thus, when 1 part by weight of vitriol and 5 parts of alcohol were simply mixed together, without special care, 10 per cent. of the acid was transformed into sulphovinic in one hour, and 26 per cent. in 24 hours. When, however, 1 part by weight of vitriol and 2 parts of alcohol were mixed with special precautions,* no sulphovinic acid was formed in an hour, and only a small percentage of the vitriol was transformed in 24 hours, although the larger proportion of vitriol would favour the reaction. Whether it progress slowly or quickly, however, the reaction finally reaches the same limit. The extreme percentage of the sulphuric acid transformable by slow or quick reaction, is 59 per cent. By heating to 100°, 56 per cent. may be transformed in one hour. This temperature should not be long maintained, however, since in one experiment, after heating the mixture for ten hours at 100°, only 42 per cent. was transformed, the retrogression being caused by the formation of ordinary ether.

If the temperature be raised to 145°, this formation of ether will be still more abundant. At 160°—170°, ethylene is also formed. It is advisable, however, in preparing sulphovinic acid, to avoid the formation of these other bodies; the temperature should, therefore, be raised to 100°, and kept at that point for a few seconds only.

II. *Action of Water upon the Sulphovinates.*—The reason that only 59 per cent. of the sulphuric acid is convertible into sulphovinic acid is

* It is not stated what these were, but they probably consisted in keeping the mixture cool, and adding the one substance to the other in small quantities at a time.

that, at that point, an equilibrium is established between the alcohol, the sulphuric acid, the sulphovinic acid, and the water, just as in the formation of other compound ethers. This limit is not the same for equivalents of all acids, since bibasic organic acids form two compound ethers, the one neutral and the other acid. With such acids the acidity is reduced to 34 per cent. of its original value, whereas in the case of sulphuric acid, which forms only the one compound acid ether, viz., sulphovinic acid, the acidity is reduced to 70 5 per cent. of the original. But, though the limit is not the same, the general phenomena are similar.

When the equilibrium is once established between the alcohol, the acid, the compound ether, and the water, it is not affected by temperature so long as no new compounds, such as ordinary ether or ethylene, are formed. The limit of production of sulphovinic acid is, of course, modified if, instead of starting with equivalent quantities of acid and alcohol only, we employ more water than the vitriol naturally contains. The effect of adding one equivalent of water to equivalent quantities of vitriol and alcohol is shown in the following table, where I stands for a mixture of the last two only, and II for the same mixture with one equivalent of water in addition. The numbers represent the percentage of sulphuric acid converted into sulphovinic acid in the times given above them:—

	40 hours.	90 hours.	20 days.	147 days.
I	56·0	57·4	59·0	58·8
II	13·2	21·2	41·2	54·8

Alcohol containing as much as 25 per cent. of water did not furnish more than 8 per cent. in a month.

Just as water prevents the formation of sulphovinic acid, so the addition of water to the acid or its salts causes decomposition, and the reproduction of alcohol and sulphuric acid. This point must be particularly borne in mind if it be desired to preserve the sulphovinates. The acid is more prone to decompose when in solution than its salts, since the solutions of these may be evaporated even to the crystallising point. But the solutions of the salts must never be kept longer than necessary, for the decomposition which sets in slowly at first progresses in a geometrical ratio, for the following reason. The sulphuric acid set free at the beginning of the decomposition combines with its equivalent of base, setting free sulphovinic acid. This is not only more liable to change than the salt, but it is produced in larger and larger proportions in equal intervals of time, since, as each equivalent of sulphovinic acid breaks up, it sets free one equivalent of sulphuric acid, which reacts upon two equivalents of sulphovinate, giving rise to two equivalents of sulphovinic acid. These in their turn decompose, yielding two equivalents of sulphuric acid, and so on. It is necessary, then, in order to diminish this inevitable decomposition, to keep the solutions of the sulphovinates neutral or slightly alkaline, which is best done with sodium carbonate. Even when the salts are obtained in the crystalline state, they are liable to be changed by the water of crystallisation. No anhydrous sulphovinates have ever come under the author's notice. The decomposition of the crystals always proceeds thus:—

Some of them begin to effloresce; the neighbouring ones become acid from the action of the eliminated water, and the decomposition then proceeds every day more rapidly, although some specimens will last for years, whilst others are decomposed in a few weeks. In order to prevent this decomposition as much as possible, the crystals should be carefully freed from the mother-liquor and kept at an unvarying temperature. B. J. G.

New Derivatives of Propyl (continued). By A. Cahours (Compt. rend., lxxvi, 1383—1387).

Glucinum-propyl.—Mercury-propyl was acted upon by thin plates of metallic glucinum in a sealed tube at 130°—135°. The glucinum disappeared and the mercury collected at the lower part of the tube. The glucinum-propyl was distilled in an atmosphere of carbon dioxide, and, after rectification, a colourless liquid was obtained boiling at 244°—246°. In contact with air it gives off dense fumes which sometimes take fire. At −17° it is a thick oil. Water decomposes it with violence, forming large quantities of gas and glucinum hydrate. The author has confirmed his statement made thirteen years ago, as the result of an experiment with very little material, that glucinum-ethyl may be prepared in a similar way to the above. It is a colourless, limpid liquid boiling at 185°—188°. It behaves in the air like glucinum-propyl, and with iodine like aluminium-ethyl. Water or alcohol decomposes it, even at zero.

Silico-propionic Ether.—When 24 parts of anhydrous propyl alcohol were slowly poured into 17 parts of silicium chloride, phenomena occurred similar to those observed by Ebelmen with the chloride and ethyl alcohol. *Tetrapropoxyl silicide*, $Si(OC_3H_7)_4$, was obtained in the form of a colourless, limpid liquid, boiling at 225°—227°, and of sp. gr. 0·915 at 18°. When left in water or exposed to a moist atmosphere, it deposits gelatinous silica.

Silico-propionic Monochlorhydrin.—Ebelmen named the series lying between silicium chloride, $SiCl_4$, and tetrethoxyl silicide, $Si(OC_2H_5)_4$, *chlorhydrins.* When one part of silicium chloride and 4·5 parts of the tetrapropoxyl silicide were heated in a sealed tube at 160° for three or four hours, *silico-propionic monochlorhydrin* (or *monochloropropoxyl silicide*) was obtained by the following reaction:—

$$SiCl_4 + 3Si(OC_3H_7)_4 = 4[Si(OC_3H_7)_3Cl].$$

It boils at 208°—210°, and its sp. gr. = 0·98.

Silicopropionic Dichlorhydrin.—When (a.) one part of silicium chloride and 2·8 parts of the ether last described were heated in a sealed tube at 160°—165°, or (b) when one part of the chloride and 1·52 part of tetrapropoxyl silicide were similarly treated at 170°, *silicopropionic dichlorhydrin* (or *dichloropropoxyl silicide*) was formed thus:—

$$(a.)\ SiCl_4 + 2[Si(OC_3H_7)_3Cl] = 3[Si(OCH_7)_2Cl_2].$$
$$(b.)\ SiCl_4 + Si(OC_3H_7)_4 = 2[Si(OC_3H_7)_2Cl_2].$$

It is a colourless, limpid fluid, boiling at 185°—188°, of sp. gr. 1·028.

Boropropylic Ether.—When a current of pure boron chloride was passed very slowly into anhydrous propyl alcohol at 0°, the gas was absorbed, and two layers of liquid were formed. The upper layer after purification yielded *boropropylic ether* (or *propoxyl boride*), $Bo(OC_3H_7)_3$, which is a colourless, mobile liquid, sp. gr. at 16° = 0·867, boiling at 172°—175°. When applied to the tongue it causes a burning sensation and leaves a slightly bitter after-taste. Alcohol, ether, and water dissolve it readily. The aqueous solution decomposes, boric acid being deposited. Propoxyl boride burns with a green-edged flame, dense fumes of boric acid being at the same time evolved.

Propyl Allophanate.—Ethyl allophanate was obtained by Hofmann by acting on urea with absolute alcohol, urethane or ethyl carbamate being formed at the same time. When propyl alcohol was substituted by the author for ethyl alcohol in the above experiment, propyl allophanate was obtained in the form of pearly laminæ slightly soluble in cold water, and very soluble in hot water and in alcohol. It melts at 150°—160°, and has the composition $C_5H_{10}N_2O_3$. *Propyl-urethane* was formed at the same time, and was separated from the excess of urea by digesting with ether, evaporating the ethereal solution to dryness, taking up with a little water, and evaporating the aqueous solution. Propyl-urethane crystallises in long, colourless, shining prisms, readily soluble in water or alcohol. It melts at 51°—53°, and boils at 194°—196°. Its formation is thus represented:—

$$CH_4N_2O + C_3H_7.OH = NH_3 + NH_2\,CO.OC_3H_7.$$

B. J. G.

Carbonyl Compounds of Isobutyl. By E. MYLIUS (Deut. Chem. Ges. Ber., vi, 312—316).

Isobutyl Sulphethyldioxycarbonate, $CO\left\{\begin{matrix}SC_2H_5\\OC_4H_9\end{matrix}\right.$, is produced by adding isobutyl chlorocarbonate, drop by drop, to sodium ethylmercaptide and heating the product in a water-bath. It is a very refractive liquid boiling at 190°—195°, and smelling like mercaptan and ethyl carbonate. Cold alcoholic potash decomposes it with formation of mercaptan and glistening needles, consisting probably of potassium isobutyl carbonate. By heating it with an excess of potash it yields mercaptan, isobutyl alcohol, and potassium carbonate. Heated with alcoholic ammonia to 100° it is decomposed into mercaptan and isobutyl carbonate. *Ethyl sulphisobutyldioxycarbonate*, $CO\left\{\begin{matrix}SC_4H_9\\OC_2H_5\end{matrix}\right.$, was prepared from sodium isobutyl mercaptide and chlorocarbonic ether; it boils at 190°—193°, and is only slowly decomposed by ammonia at 100° into ethyl carbamate and isobutyl mercaptan. Cold alcoholic potash acts on it, potassium ethyl carbonate being formed, whilst an excess of potash yields potassium carbonate, alcohol, and isobutyl mercaptan. By heating it with an alcoholic solution of potassium sulphhydrate the following reaction is produced:—

$$CO \left\{ \begin{matrix} SC_4H_9 \\ OC_2H_5 \end{matrix} \right. + 2KSH + 2H_2O = C_4H_9.SH + C_2H_5.OH + 2H_2S + K_2CO_3.$$

Isobutyl iodide acts on potassium trisulphocarbonate only at 130°, the principal reaction taking place according to the equation:—

$$C_4H_9I + 3H_2O + K_2(S_2CS) = C_4H_9.SH + HI + K_2CO_3 + 2H_2S.$$

At the same time, some *isobutyl trisulphocarbonate* is formed, an orange-red oil boiling at 285°—289°, and having only a faint smell. The reactions of this body resemble those of its lower homologues. Sodium isobutyl trisulphocarbonate is produced by combining sodium isobutyl-mercaptide with carbon sulphide; it is soluble in water and alcohol, and forms yellow, warty needles. Water acts slowly on it at the common temperature, but quickly at 100°, decomposing it into acid sodium carbonate, hydrogen sulphide, and isobutyl mercaptan. By adding sulphuric acid to its aqueous solution, an oil separates out, consisting probably of the free acid, which, however, was found to be too unstable to be analysed.

C. S.

Polymerisation of Hydrocarbons.—Trimethylcarbinol. By A. Buttlerow and B. Gorjainow (Deut. Chem. Ges. Ber., vi, 561).

The authors find that no polymerisation of ethylene takes place when it is heated with sulphuric acid or boric fluoride to 200°, but that a considerable quantity of alcohol is formed at 160° by the sulphuric acid. Propylene and isobutylene on the contrary are polymerised both by sulphuric acid and by boric fluoride at the ordinary temperature; this accounts for the fact that in preparing trimethylcarbinol by the action of dilute sulphuric acid on isobutylene, a neutral oil is always produced. This can be separated by fractional distillation into two portions, one of which boils at 173°—176°, and consists of isobutylene, $C_{12}H_{24}$; the other passes over at 176°—215°, so that dibutylene would not seem to be formed in this reaction.

Buttlerow finds that the crude trimethylcarbinol prepared according to Linnemann's method by the action of acetic acid and moist silver oxide on isobutyl iodide is a mixture of isobutylic alcohol and trimethylcarbinol, so that the yield of the latter after purification is not so large as stated.

C. E. G.

Preparation of α-Sulphopropionic Acid. By A. Kurbatow (Deut. Chem. Ges. Ber., vi, 563).

The author prepared this acid by treating propionic acid with chlorosulphuric acid, $HClSO_3$, the mixture being gently warmed to complete

the reaction; it was then diluted with water and the unaltered propionic acid separated by distillation. In order to purify the new acid, it was repeatedly converted into a lead salt by treatment with lead oxide, and then decomposed by sulphuretted hydrogen. The free acid is an uncrystallisable syrup, easily soluble in water and in alcohol. The *barium salt*, $C_3H_4BaSO_5 + 2H_2O$, crystallises in colourless, glistening scales, which are sparingly soluble in water, more easily in alcohol. The *calcium salt*, $C_3H_4CaSO_5 + 2H_2O$, is obtained as a flocculent precipitate on adding alcohol to its aqueous solution. The same acid is produced by treating ethyl α-chloropropionate with ammonium sulphite.

C. E. G.

Preparation of Valerianic Acid on the Large Scale. By Is. PIERRE and E. PUCHOT (Ann. Chim. Phys., [4], xxix, 228—246).

PURE valerianic acid is conveniently prepared in quantity by adding very gradually a cold mixture of 1400 grams of sulphuric acid, and 800 grams of water, to a mixture of 3500 grams of water, 1000 grams of powdered potassium dichromate, and 1 litre of pure amyl alcohol. The liquid must be well agitated, and kept at a temperature of 11°—12°. The light layer which separates out on standing is distilled, and the portion boiling between 175°—192°, and consisting chiefly of amyl valerate, collected separately. 400 grams of potash and 200 grams of water are then gently heated in a retort, and 1000 grams of the valerate very gradually added, and when the reaction is finished, some more water is added, the regenerated amyl alcohol is distilled off, and the residue distilled with dilute sulphuric acid.

Pure valerianic acid boils at 178° under a pressure of 760 mm. A layer of 20 centim. gave in Soleil's saccharometer a deviation of 5° to the right; the same thickness of anhydrous amyl alcohol was found by the authors in previous experiments to deviate 8·5° to the left, but when it was saturated with water, the deviation increased to 11°, or about 2·5° more.* The specific gravity of the pure acid is 0·947, at 0°, 0·8972 at 54·65, 0·8542 at 99·9 and 0·8095 at 147·5°. From these

* According to Pedler (*Chem. Soc. J.*, [2], vi, 74), *active* valerianic acid turns the plane of a polarised ray 43° to the right in a tube 50 c.m. long, which is equivalent to a deviation of 17·2° for a column 20 c.m. long, whereas Pierre and Puchot find only 5°. Hence it seems probable that their valerianic acid was a mixture of the active and inactive acids; but they take no account of the existence of these isomeric modifications, and make no reference to Pedler's researches, or to those of Erlenmeyer and Hell, who found for the active acid a rotatory power of 48·7° for 50 c.m., or 19·5° for 20 c.m. (see this Journal, 1872, p. 244). The rotation which Pierre and Puchot assign to amylic alcohol, viz., 8·5° for a column 20 c.m. long is greater than that found by Pedler for the active alcohol (17° for 50 c.m., or 6·8° for 20 c.m.); but as the authors speak of this determination as obtained "dans des recherches antérieures," there is no certainty that the amylic alcohol with which it was made was the same as that used for the preparation of the valerianic acid described in the present communication.—ED.

1·18 of lime-soap, and 0·957 of calcium sulphate, the solubility of the last substance increasing with the temperature.

The author has also found that the metallic and earthy sub-soaps which impregnate the fibres of wool readily form an emulsion with water containing glycerin, and points out the importance of the use of glycerin in the manufacture of woollen textures. J. R.

Monobasic Calcium Saccharate. By R. Benedict (Deut. Chem. Ges. Ber., vi, 413—415).

The existence of this compound has been doubted, but it can be readily obtained by dissolving an excess of lime in a solution of sugar, and adding magnesium chloride. Magnesium hydroxide is precipitated, and the monobasic calcium-compound formed, which is precipitated and washed with alcohol. Dried in a vacuum it forms a brittle, translucent mass, having the composition $C_{12}H_{20}CaO_{11} + 2\,aq$. It loses its water at 100°, and forms with water a clear solution, which becomes turbid when heated, the tribasic saccharate separating out. A magnesium saccharate could not be obtained. C. S.

New Researches on Aldol. By A. Wurtz (Compt. rend., lxxvi, 1165—1171).

Further experiments confirm the author's statements (this Journal [2], x, 808) respecting the preparation, constitution, and functions of this body. The reaction which furnishes it is not completed for several days at 15°—20°, and the temperature must not fall below this point. The neutralisation with sodium carbonate should be made as soon as the liquid attains a fawn colour. If a longer time elapses, the neutralisation is followed by the precipitation of a quantity of resinous matter. Recently distilled aldol is liquid, but it gradually becomes viscid, giving out heat at the same time. Thus, a quantity of freshly distilled aldol, being at a temperature of 11°, gradually rose to 54° in one hour, after which it slowly cooled till, at the end of three hours more, its temperature was 30°. It was then viscid. Aldol when viscid bears, probably, the same relation to liquid aldol that paraldehyde does to aldehyde, although the polymerised aldol would naturally not be so stable as paraldehyde. Aldol kept for several hours at 60°, in a current of dry air, loses water, and on cooling, appears as a colourless, transparent, vitreous solid, insoluble in water. A great lapse of time will produce the same result. When aldol is treated with moist silver oxide, the mixture becomes hot, and metallic silver is formed; and if the liquid be then boiled, filtered, and concentrated, a silver salt separates out in long, interlaced crystals, which, when decomposed with sulphydric acid, furnish the β-oxybutyric acid of Wislicenus and Markownikoff. This acid is derived from aldol thus:—

$$\begin{matrix} CH_3 \\ CHOH \\ CH_2 \\ CHO \end{matrix} + O = \begin{matrix} CH_3 \\ CHO \\ CH_3 \\ COOH. \end{matrix}$$

Aldol is, therefore, its aldehyde. When a current of ammonia is passed into an ethereal solution of aldol, a syrupy, colourless body is precipitated, which dries *in vacuo* to an amorphous, transparent, semi-resinous mass. It is very soluble in water, and has an odour resembling that of ammonia-aldehyde, of which it is, indeed, the aldol analogue, its composition being that of aldol with one atom of hydrogen replaced by ammonium. The hydrogenation of aldol is effected as follows:—A 4 per cent aqueous solution of aldol is treated, at zero, with a sodium amalgam containing 5 per cent. sodium, and the soda formed is continually neutralised with hydrochloric acid. When the reaction, which is very slow, is complete, the liquid is shaken up with ether, from which it is then separated, and evaporated at 40°. The residue is treated with alcohol, which leaves behind the greater part of the sodium chloride. This is repeated with the evaporated alcoholic solution. The alcohol is then distilled off, and, by rectification, a butyl-glycol is obtained, boiling at 201°—203°, identical with that obtained by Kekulé as a secondary product in the hydrogenation of aldehyde. Its formation may be expressed thus:—

$$CH_3-CH(OH)-CH_2-CHO+H = CH_3-CH(OH)-CH_2-CH_2(OH).$$

When a current of hydrochloric acid gas is passed at 10° into the bottom of a concentrated aqueous solution of aldol, the latter becomes yellow, and a thick liquid, insoluble in water, is deposited, containing probably monochloraldol, CH_3—CHCl—CH_2—CHO.

B. J. G.

Action of Chlorine on Isobutyric Aldehyde.

By G. A. BARBAGLIA (Deut. Chem. Ges. Ber., vi, 317).

A STREAM of chlorine was passed into refrigerated isobutyric aldehyde until it had absorbed its own weight of the gas, and the product was treated with marble and water, after which the aqueous liquid was separated from the supernatant oily fluid, and distilled. The distillate separated into two layers, the lower stratum consisting of isobutyric aldehyde together with a chlorinated substance, and the upper stratum consisting of an aqueous solution of both these substances. By fractionating the lower stratum, the chlorinated substance was isolated and was found to be a colourless highly refractive liquid, the vapour of which is very irritating to the eyes and mucous membrane. It boils at 120°, and its analysis and vapour-density led to the formula C_3H_5ClO. Caustic soda communicates to it an intense but evanescent red coloration. This reaction is not produced by carbonated alkalis at the ordinary temperature. Ammonia, however, similarly attacks it in the cold, and alkaline sulphides, hydrosulphates, cyanides, and sulphocyanates react similarly when boiled with the substance.

The author considers it probable that an atom of carbon is eliminated as methyl chloride, and he appears inclined to regard the compound just described as a monochloro-derivative of propionic aldehyde, this view being somewhat strengthened by the fact that it reduces

silver salts, and yields with sodium bisulphite a crystallised compound having the composition $C_3H_5ClO.NaHSO_3$.

When one part of the substance C_3H_5ClO is heated with four parts of nitric acid, an energetic reaction takes place, and a greenish solution is produced, having an odour suggestive of chloropicrin, and yielding to ether a white substance crystallising in prisms or tables. Its composition is represented by the formula C_3H_4ClNO, and it melts at 110°, a somewhat higher temperature causing it to sublime with partial decomposition. Water, alcohol, and ether dissolve it readily, the solution in the two last-named solvents being neutral; the aqueous solution is, however, slightly acid, the acidity, which appears to be due to the liberation of hydrochloric acid, becoming greater on standing, or on the application of heat. When heated for some time to 100° with water, it is entirely decomposed, a crystalline substance melting at 171° being produced.

T. B.

The Action of Sulphuric Acid on Chloral. By J. Grabowski (Deut. Chem. Ges. Ber., vi, 225—226).

Those chemists who have hitherto studied the action of sulphuric acid on chloral, appear to have quite overlooked the fact that the two substances readily combine, for chloral when mixed with fuming sulphuric acid solidifies, after a short time, to a white crystalline mass, which contains neither insoluble chloral nor chloralide, but which is a compound of chloral and sulphuric acid, $C_8H_6Cl_{12}O_{11}S_2$. It is not changed by cold water, but is readily decomposed by warm water, potassium hydrate, or alcohol, in the latter instance with formation of chloral alcoholate. From ether, in which it is very soluble, it crystallises in needles.

On passing the vapour of sulphuric anhydride into chloral, the whole solidifies to a mass of needles differing from the compound just described. It crystallises from alcohol apparently unchanged, is insoluble in cold water, but is decomposed by warm water and by a solution of potassium hydrate. On being gently heated it melts, and separates into two layers, whilst at a higher temperature it evolves hydrochloric acid and leaves an oil which does not solidify and is not acted upon by water.

C. E. G.

Action of Glacial Acetic Acid on Chloral. By V. Meyer (Deut. Chem. Ges. Ber., vi, 449).

The product of this action is not an acid, as Hübner has conjectured, but is either chloral hydrate (melting at 57°) or an isomeride thereof (melting at 80°), according as the crystals are deposited after slow or quick evaporation.

Trimethylamine dropped on chloral free from hydrochloric acid produces a hissing sound, and gives rise to a non-nitrogenous product, the investigation of which is not yet complete. Water produces a

well-crystallised compound with the resulting white amorphous body; alcoholic ether gives rise to chloral alcoholate melting at 44°—46°.

C. R. A. W.

Preparation of Potassium Sulphocyanate. By W. Skey (Chem. News, xxvii, 179).

Sulphur, when deprived of adhering air by placing it for a few minutes into boiling water, readily acts upon a solution of potassium cyanide at the ordinary temperature, forming sulphocyanate. The operation must be carried on in an air-tight vessel. It will be seen that this method avoids much of the labour and expense required by the usual plan, which necessitates several purifications of the sulphocyanate formed by fusing together potassium ferrocyanide and sulphur.

B. J. G.

Preparation of Nitriles. By O. Witt (Deut. Chem. Ges. Ber., vi, 448).

Dry ferrocyanide of potassium may be used instead of cyanide for the production of nitriles, *e.g.*, propionitrile (from potassium ethyl sulphate), α-napthoic nitrile, benzonitrile, &c., a purer product being obtained with greater ease.

C. R. A. W.

The Nitrile of Ethylglycollic Acid. By L. Henry (Deut. Chem. Ges. Ber., vi, 259—263).

When equal molecules of *ethylglycollamide*, $(C_2H_5O)CH_2.CO(NH_2)$, and phosphorus pentoxide are heated, the *nitrile* of *ethylglycocollic acid*, $(C_2H_5O)CH_2.CN$, distils over. It is a limpid, mobile liquid, boiling at 134°—135°, and possessing an agreeable odour resembling that of ethyl formate. Like other nitriles, it combines with gaseous hydrobromic acid, forming a crystalline compound which is insoluble in ether and resolved by water into its components. Aqueous acids or alkalis convert the nitrile into ethylglycollic acid. The same nitrile is produced by distilling the amide with phosphorus pentachloride; the product contains a combination of the nitrile with phosphorus trichloride. This body, which could not be obtained in a pure state, is a liquid, fuming in the air, and boiling at about 100°—105°. Henke has already obtained similar compounds of acetonitrile and propionitrile. The nitrile of ethylglycollic acid is also formed, but mixed with secondary products, by distilling the amide with phosphorus pentasulphide.

C. S.

A Compound of Allyl Cyanide and Ethylic Alcohol. By A. Rinne (Deut. Chem. Ges. Ber., vi, 389).

When a mixture of allyl iodide and alcohol is digested with excess of potassium cyanide, the allyl cyanide first produced combines with the

alcohol, forming a compound having the formula $C_4H_5N.3C_2H_6O$. This substance may be isolated by fractional distillation, and forms a liquid having an agreeable odour resembling that of allyl cyanide, and boiling at 173°—174°. Digestion with potash decomposes it, with formation of crotonic acid, ammonia, and alcohol, no ethylamine being produced.

T. B.

Chloracetylurea. By D. TOMMASI (Compt. rend., lxxvi, 640—642).

THIS compound is produced by the action of chloracetic chloride on urea—

$$CON_2H_4 + C_2H_2ClOCl = HCl + CON_2H_3(C_2H_2ClO).$$

Reaction sets in spontaneously soon after the two substances are mixed, and is accompanied by evolution of heat; to complete it, the mass must ultimately be warmed for several hours on the water-bath. The product is then washed with cold water, and several times crystallised from alcohol. Chloracetylurea forms colourless needles insoluble in cold, slightly soluble in hot water, readily soluble in hot alcohol. It does not yield a precipitate either with mercuric nitrate or silver nitrate.

When a small quantity (·5 mgrm.) is placed upon the tongue it gives rise at first to no particular sensation, but after the lapse of two or three minutes a burning taste, accompanied by sharp pain, is experienced in the larynx. These symptoms ordinarily disappear at the end of an hour.

H. E. A.

Glycolyl-sulphur-urea. By J. VOLHARD (Ann. Chem. Pharm., clxvi, 383).

BY acting with sulphur-urea on monochloroacetic acid, Maly obtained a compound which he regards as *monochloracetyl-sulphur-urea*—

$$CS\left\langle\begin{array}{l}NH_2\\NH_2\end{array}\right. + CO.OH.CH_2Cl = H_2O + CS\left\langle\begin{array}{l}NH_2\\NH.CO.CH_2Cl.\end{array}\right.$$

On treating this body with ammonia or baryta-water, he obtained glycolyl-sulphur-urea or the sulphur-derivative of hydantoin—

$$CS\left\langle\begin{array}{l}NH_2\\NH.CO.CH_2Cl\end{array}\right. + NH_3 = NH_4Cl + CS\left\langle\begin{array}{l}NH.CH_2\\ \qquad\;\, |\\NH.CO.\end{array}\right.$$

The author has been engaged on the same subject and found, before Maly's publication, that by the above reaction no monochloracetyl-sulphur-urea is formed, but the isomeric *hydrochloride* of *glycolyl-sulphur urea*. This compound evolves hydrochloric acid when treated with sulphuric acid, and combines with platinic chloride, forming the compound, $2(C_3H_4N_2OSHCl).PtCl_4$, crystallising in small acicular plates. On adding silver nitrate to a solution of the hydrochloride, the chlorine

is completely precipitated; and ammonia, alkalis, alkaline earths, and their carbonates precipitate from the solution glycolyl-sulphur-urea, which crystallises from hot water or dilute alcohol in long, glistening needles, and combines readily with hydrochloric acid, reproducing the original compound. By acting with one molecule of sulphur-urea on two molecules of monochloracetic acid, another body is produced, forming a hydrochloride which is decomposed by water.

C. S.

Mustard Oils [Isosulphocyanic Ethers or Sulphocarbimides].

By Eugen Sell (Deut. Chem. Ges. Ber., vi, 322).

When ethyl-sulphocarbimide is treated with dry chlorine, a very energetic action takes place, carbon disulphide and other products being formed. If, however, the sulphocarbimide be diluted with an equal volume of ether and the temperature be moderated by external cooling, the action of chlorine is much less energetic. After the action has continued for some time, the whole solidifies to a yellow mass, which dries up under the air-pump to a yellowish-white powder. The analysis of this substance did not lead to satisfactory results, but when treated with soda-solution it is converted into a brown oil, sulphur being at the same time separated. The oil becomes crystalline on standing, and, after having been submitted to pressure and crystallised from alcohol, the new substance forms fine six-sided tables and prisms, which gave numbers corresponding with the formula $C_6H_{10}S_2N_2O$. It may be regarded as a compound of two molecules of ethyl-sulphocarbimide and one of oxygen, $\left(\left.\begin{matrix}(CS)''\\C_2H_5\end{matrix}\right\} N\right)_2O$. It melts at 42°, is almost insoluble in water, but soluble in ether and easily soluble in alcohol. Nitric acid oxidises it, with production of red fumes, and platinum chloride unites with it forming an amorphous red substance. When it is treated with ammonium sulphide, sulphur is liberated, and the filtrate yields on evaporation a crystalline substance melting at about 60°. This substance did not appear to be ethyl-urea.

The author finds that bromine and iodine act on ethyl-sulphocarbimide, and he purposes to extend his investigations to the other alcoholic sulphocarbimides.

T. B.

Propenediamine. By A. W. Hofmann (Deut. Chem. Ges. Ber., vi, 308—311).

Propene dibromide is acted upon by alcoholic ammonia in exactly the same way as ethene bromide. Of the products formed, only *propenediamine* was examined; this base obstinately retains water like the ethene-base, and can be obtained anhydrous only by heating it with sodium. It boils at 119°—120°, and has at 15° the specific gravity 0·878; it is so very hygroscopic that a glass-rod moistened with it fumes in the air; it also attracts carbon dioxide very rapidly. The hydrate has the composition, $2C_3H_6(NH_2)_2 + H_2O$, and boils at the same temperature as the anhydrous base. *Propenediamine hydro-*

chloride, $C_3H_6(NH_2)_2,2HCl$, forms long, white needles; it is very hygroscopic and very freely soluble in water, but less in alcohol. The platinum double salt is formed only in concentrated solution; it crystallises in beautiful four-sided plates. The hydrobromide and hydriodide have great resemblance to the hydrochloride; the nitrate could not be obtained in crystals.

C. S.

The Phosphines of the Propyl, Butyl, and Amyl Series.

By A. W. HOFMANN (Deut. Chem. Ges. Ber., vi, 292—301).

IN several former communications the author has described the phosphines of methyl and ethyl, which he obtained by heating the corresponding iodides with phosphonium iodide and zinc oxide to 150°. He has since found that these compounds, as well as the phosphines of isopropyl and isobutyl, are more conveniently prepared by heating the mixture only to 100° for 5—6 hours. The separation of the primary bases from the secondary ones is very simple, as the hydriodides of the former are readily decomposed by water, but those of the latter only by an alkali.

Isopropylphosphine, $(C_3H_7)PH_2$, is a light, limpid, very refractive liquid, boiling at 41° and possessing a most penetrating odour. It combines with sulphur and with carbon sulphide, forming uncrystallisable compounds. It readily absorbs oxygen and takes fire on a hot summer's day.

Di-isopropylphosphine, $(C_3H_7)_2PH$, boils at 118°; it absorbs oxygen more quickly than the primary base; a drop put on filter-paper taking fire and blackening the paper slightly without inflaming it. On heating it with isopropyl iodide to 120°, it yields *tri-isopropylphosphine hydriodide*, $(C_3H_7)_3P.IH$, which forms large crystals and is readily soluble in water and alcohol but insoluble in ether. The free base is a liquid, forming with carbon sulphide a red crystalline compound. *Tetrisopropylphosphonium iodide*, $(C_3H_7)_4I$, is produced by combining the tertiary base with isopropyl iodide at 100°; it crystallises from water in cubes or octohedrons.

Isobutylphosphine, $(C_4H_9)PH_2$, boils at 62° and di-isobutylphosphine, $(C_4H_9)_2HP$, at 153°. Both are liquids, having the general properties of the phosphines. The secondary base combines with isobutyl iodide at 100°, forming a beautiful crystalline mass of *tri-isobutylphosphine iodide*. The free base boils at 215°; it combines with isobutyl iodide, but the tetrisobutylphosphonium iodide could not be obtained in a pure state. As the tertiary phosphorus bases and phosphammonium compounds of the lower members of the series are also produced by heating the alcohols with phosphonium iodide, isobutyl alcohol was heated with the latter body, but no phosphines were formed, the alcohol being decomposed with formation of hydrocarbons.

Amylphosphine, $(C_5H_{11})PH_2$.—The phosphines of amyl are but slowly formed at 100°, but readily 140°—150°. The primary base boils at 106°—107° and absorbs oxygen with evolution of heat. *Diamylphosphine*, $(C_5H_{11})_2PH$, boils at 210°—215°; a drop on filter-paper is oxidised, with the formation of dense, white phosphorescent

fumes, without taking fire. Triamylphosphine boils at about 300°, but could not be obtained in the pure state. In one experiment some *tetramylphosphonium iodide* was formed, which, on addition of an alkali, separated as a viscid liquid, but became crystalline on standing for some months.

When amyl alcohol and phosphonium iodide are heated to 150°, they yield amyl iodide and hydrogen phosphide, whilst at 170°—180° gaseous hydrocarbons are formed.

Methylisopropylphosphine, $\left.\begin{matrix}CH_3\\C_3H_7\end{matrix}\right\}PH$, is obtained as hydriodide by heating the primary propyl base with methyl iodide to 100°. The free base boils at 78°—80°. *Isopropylisobutylphosphine*, $\left.\begin{matrix}C_3H_7\\C_4H_9\end{matrix}\right\}PH$, is formed by heating isopropylphosphine and butyl iodide to 130°; it boils at 139°—140°. By heating it with ethyl iodide to 100° it yields *ethyl-isopropyl-isobutylphosphine*, a very oxidisable liquid boiling at about 190°.

Methyl tri-isobutylphosphonium iodide.—Methyl iodide acts on tri-isobutylphosphine with explosive violence; the crystalline product is purified by dissolving it in water, adding an alkali, and distilling off the volatile phosphines; the solution is then treated with carbon dioxide, evaporated to dryness, and exhausted with alcohol; the crystalline residue is readily soluble in water, from which it separates in fine crystals. A very similar body is *methyl-ethyl-isopropyl-isobutyl phosphonium iodide*, which was obtained by combining methyl iodide with methyl-isopropyl-isobutyl-phosphine.

C. S.

Formation of Phosphines with the Aid of Reduction-processes. By A. W. Hofmann (Deut. Chem. Ges. Ber., vi, 301—303).

The phosphines of polygenic radicals cannot be obtained by the reaction by which the phosphines of monad radicals are prepared, on account of the reducing action of hydriodic acid. Zinc oxide and phosphonium iodide act on ethene dibromide at 160°, but only ethylphosphine is produced. Chloroform is acted upon already at 100°, methylphosphine being formed. Benzylene chloride, $C_6H_5.CHCl_2$, as well as the chloride, $C_6H_5.CCl_3$, yield only the phosphines of benzyl, which, therefore, can be readily obtained pure by employing the crude product of the action of chlorine on boiling toluene. For the same reason, crude isopropyl iodide containing allyl iodide yields pure isopropylphosphine.

C. S.

Phosphinic Acids. By A. W. Hofmann (Deut. Chem. Ges. Ber., vi, 303—307).

These acids are formed by oxidising the phosphines with fuming nitric acid. The product, which always contains some phosphoric acid, is easily purified by dissolving it in ammonia and adding acetic acid and lead acetate. The filtrate is treated with hydrogen sulphide, and the

solution evaporated. *Isopropylphosphinic acid*, $PO_3(C_3H_7)H_2$, is a white mass, resembling paraffin, and melting between 60°—70°; it is soluble in water, and more freely in alcohol. *Isobutylphosphinic acid* is a very similar body, melting at 100°. *Amylphosphinic acid* is prepared by adding amylphosphine to a mixture of equal volumes of fuming nitric acid and nitric acid of sp. gr. 1·2; the fuming acid acts too violently and sets fire to the base. The acid crystallises from hot water in small, pearly, rhombic plates, melting at 160°. The silver salts of these bibasic acids are white, amorphous precipitates. The secondary phosphorus-bases of these radicals yield by oxidation with nitric acid the corresponding phosphinic acids, which could not be obtained in a state fit for analysis, nor could any of their salts be prepared in a pure state. The free acids are oily liquids, and insoluble in water.

Triamylphosphine oxide, $(C_5H_{11})_3PO$, is always formed in small quantity in the preparation of triamylphosphine; it boils above 360° and solidifies, after the phosphine has distilled over, in the neck of the retort, as a crystalline mass melting at 60°—65°. Water precipitates it from an alcoholic solution as a crystalline powder.

Methylphosphinic chloride, $P(CH_3)OCl_2$, is obtained by acting with phosphorus pentachloride on methylphosphinic acid. It is a crystalline solid melting at 32° and boiling at 163°. Water, alcohol, ammonia, and aniline act violently on it, like on other acid chlorides. *Dimethylphosphinic chloride*, $P(CH_3)_2OCl$, melts at 66° and boils at 204°. Water and alcohol decompose it, but with less violence than the preceding compound.

C. S.

Compounds of Aldehydes and Alcohols with Aromatic Hydrocarbons. By A. BAEYER (Deut. Chem. Ges. Ber., vi, 220—224).

Formaldehyde and Aromatic Hydrocarbons.—The author considers it probable that the action of cold sulphuric acid on the acetal of formaldehyde (methylal) causes the liberation of formaldehyde, which, at the moment of its formation, combines with the sulphuric acid and forms a compound analogous to the chloral sulphate which is now being studied by Grabowski. When a mixture of methylal and sulphuric acid is warmed, an odour of the aldehyde becomes perceptible, and a sublimate of the solid modification is produced. Methylal can be advantageously used, instead of formaldehyde or its acetate, for the formation of the condensed products derived from this aldehyde and aromatic hydrocarbons (*Deut. Chem. Ges. Ber.*, v, 1094).

Formaldehyde and Benzene.—A mixture of 40 grams methylal, 120 grams benzene, and 400 grams glacial acetic acid, is treated with a mixture of equal parts of glacial acetic acid and sulphuric acid, until the greater part of the benzene has separated. After the mixture has remained at rest for 24 hours, 2000 grams of sulphuric acid are gradually added, the mixture being kept cool. The whole is now left at rest for some hours, after which it is diluted with water and agitated with ether. The ethereal solution when distilled yields diphenylmethane, a hydrocarbon which appears to be identical with the hydrocarbon "I," which Zincke obtained by the action of benzyl chloride on benzene, and

at a high temperature a crystalline hydrocarbon or mixture of hydrocarbons.

Formaldehyde and Diphenylmethane.—When these substances are made to act on one another in a manner similar to that detailed above, a hydrocarbon is obtained which differs from the hydrocarbon I. It crystallises from alcohol in leaflets, melting at about 90°. Its composition may be represented by the formula—

$$C_6H_4\left\langle\begin{matrix}CH_2\\CH_2\end{matrix}\right\rangle C_6H_4, \text{ or else by}$$

$$C_6H_5—CH_2—C_6H_4—CH_2—C_6H_4—CH_2—C_6H_5.$$

Formaldehyde and Diphenyl yield a hydrocarbon which separates from chloroform in small crystals.

These results tend to show that the partial substitution of the hydrogen of benzene by hydrocarbons does not prevent the formation of condensed products with formaldehyde. When, however, one hydrogen is replaced by chlorine or bromine, the reaction takes place much less readily; and derivatives richer in chlorine, also nitrobenzene and aniline, are not acted on by formaldehyde.

Chloral and Benzene.—When the compound which the author has already obtained by the action of chloral on benzene, is boiled with alcoholic potash, it is decomposed, with formation of diphenyldichlorethylene—

$$(C_6H_5)_2CHCCl_3 = (C_6H_5)_2C.CCl_2 + HCl.$$

A crystallised compound derived from dichloraldehyde and benzene was obtained by treating them with sulphuric acid, and analogous crystalline substances were obtained from toluene and chloral, from monochlorbenzene and chloral, and from benzene and bromal. The substance derived from xylene and chloral does not appear to crystallise. Crotonic chloral may be mentioned as an instance of a high aldehyde which yields results analogous to those described in this paper.

Alcohols and Aromatic Hydrocarbons.—When alcohols are mixed with hydrocarbons and treated with sulphuric acid, they yield condensation products. Allyl alcohol and benzene yield uncrystallisable hydrocarbons boiling at a high temperature, and the same alcohol, with mesitylene, yields an oily hydrocarbon which distils at about the same temperature as mercury, and a small quantity of a solid hydrocarbon which crystallises from acetone. Ethyl alcohol and methyl alcohol yield with benzene small quantities of hydrocarbons. Perhaps these reactions are analogous to the formation of homologues of aniline as described by Hofmann.

The author is engaged in working out the results here indicated.

T. B.

On Benzene, Phenol, Monochlorobenzene, and Monobromobenzene. By A. Adrieenz (Deut. Chem. Ges. Ber., vi, 441).

The author views benzene as *methyl-pentol*, $C_5H_4.CH_2$, considering the existence of the two isomerides aniline and picoline—the occurrence of

pyridine amongst coal-tar bases—the existence of only two isomerides of monochloro-, monobromo-, and monoiod-aniline (whereas Kekulé's views indicate the existence of three such bodies)—and the existence of only two nitro derivatives of phenol—as being points in favour of this view.

Attempts to prepare an acid, $C_6H_5.CO.OH$, by oxidising very pure benzene with potassium permanganate, led to no result; formic acid was produced, and a small quantity of another acid, not sufficient for examination.

A table of the specific gravity and specific volume of pure benzene from benzoate at various temperatures is given; also a similar one for phenol.

Monochlorobenzene from benzene and from phenol were compared as to boiling points (131·5° to 131·97°, and 132·4° to 132·58° at 760 millimeters respectively); refractive index for the sodium lime (1·528 and 1·5255 at 16·4°) and specific gravity, viz.:—

From benzene.		From phenol.	
0°	1·12855	0°	1·12818
9·79°	1·11807	12·93°	1·11421
22·43°	1·10467	20·96°	1·10577
77·27°	1·04428	73·15°	1·04299

Monobromobenzene cannot be readily prepared from phenol, too little being obtained from 300 grams to determine its boiling point; that from benzene boiled at 154·86° to 155·52°, its specific gravity being—

0°	1·51768
11·46°	1·50236
20·96°	1·48977
77·76°	1·41163

and its refractive index for the sodium line 1·5595 at 15°.

Notwithstanding that these results only corroborate Kekulé's views, the author holds to his notion concerning the formula of benzene. Researches on pyridine, picoline, and pentachlorobenzene, were contemplated to decide the point, but the death of the author prevented their completion.

C. R. A. W.

Derivatives of Bromotoluene. By H. HUEBNER and P. HAESSELBARTH (Deut. Chem. Ges. Ber., vi, 410—413).

REPEATED experiments have shown that pure crystallised bromotoluene yields only two monosulphonic acids. The following derivatives were prepared in addition to those formerly described (this Journal, 1872, 696 and 1005).

(1.) *β-Parabromotoluenesulphonic Acid.* — $C_6H_3(CH_3)Br.SO_3Na + H_2O$ forms four-sided prisms.

$[C_6H_3(CH_3)Br.SO_3]_2Pb + 3H_2O$ crystallises in white needles.

$C_6H_3(CH_3)Br.SO_2Cl$ crystallises from chloroform in plates having a strong odour, and melting at 35°.

$C_6H_2(CH_3)(NO_2)Br.SO_3H$ crystallises from ether in small plates

having a very bitter taste. $(C_6H_2(CH_3)(NO_2)Br.SO_3)_2Ba + 2H_2O$ forms small, soluble, yellowish needles.

$[C_6H_2(CH_3)(NO_2)Br.SO_3]_2Pb + 3H_2O$ is very soluble, and crystallises in long needles. $(C_6H_2(CH_3)(NO_2)Br.SO_3)_2Cu + 6H_2O$ forms microscopic, light-green four-sided prisms.

$C_6H_2(CH_3)(NO_2)Br.SO_3Ag$ forms microscopic needles.

$[C_6H_2(CH_3)(NO_2)Br.SO_3]_2Sr + 7H_2O$ crystallises in soluble yellowish needles. The sodium salt is so soluble that it does not crystallise well.

(2.) *α-Parabromonitrotoluenesulphonic Acid* forms small, yellowish, deliquescent needles. Its salts exist in two forms, differing probably by the amount of water of crystallisation. $(C_6H_2(CH_3)(NO_2)Br.SO_3)_2Ba + H_2O$ forms either fine needles or compact crystals resembling salammoniac. $[C_6H_2(CH_3)(NO_2)Br.SO_3]_2Pb + 2\frac{1}{2}H_2O$ crystallises in brilliant colourless octohedrons or in thin needles. $[C_6H_2(CH_3(NO_2)Br.SO_3]_2Sr + 5H_2O$ forms fan-shaped needles.

(3.) *β-Parabromosulphobenzoic Acid* is obtained by oxidising the corresponding bromotoluene-sulphonic acid.

$C_6H_3Br(SO_3K)CO_2H + H_2O$ forms long needles.

$C_6H_3Br(SO_3BaCO_2) + \frac{1}{2}H_2O$ crystallises in thin glistening plates. $C_6H_3Br(SO_3PbCO_2) + 2H_2O$ forms small, brilliant needles, and the calcium-salt very soluble needles.

C. S.

On the Dinitro-derivatives of the Higher Homologues of Benzene. By A. Rommier (Bull. Soc. Chim. [2], xix, 434—437).

The author some time ago obtained from coal-oil two xylenes, one of which was soluble in ordinary sulphuric acid, the other insoluble. The soluble xylene gave, by treatment with nitric acid, two dinitro-compounds the mixture of which melted at 61°.

These two bodies recrystallised from alcohol, were examined by Des Cloiseaux. The less soluble α-dinitroxylene formed thin plates belonging to the monoclinic system; the more soluble β-dinitroxylene gave rhombic prisms belonging to the triclinic system. But the author has been unsuccessful in his attempts to reproduce the latter compound, and on recrystallising a portion which had been kept in reserve, it was transformed into the α-dinitroxylene.

It seems, therefore, that there is but one dinitro-compound corresponding to the xylene which is soluble in sulphuric acid.

By the action of ordinary sulphuric acid upon coal-oil, two xylenes, two cumenes, and two cymenes are obtained.

I. Hydrocarbons insoluble in sulphuric acid.

Xylene boiling at 139°—140°. Its dinitro-compound melts at about 92°; it crystallises, according to Des Cloiseaux, in rhomboidal prisms of the monoclinic system. It therefore does not agree with the dinitromethyltoluene of Fittig.

Mesitylene, boiling at 165°—167°, the most abundant of the series, has already been examined by Fittig.

Cymene.—The boiling point of this hydrocarbon has not been determined, in consequence of the impossibility of obtaining it pure, but it

probably lies near to 196°. Dinitrocymene is but slightly soluble in boiling alcohol, almost insoluble in cold alcohol, from which it is deposited in very small colourless crystals which, according to M. des Cloiseaux, are oblique rhombic prisms. It melts at 205°, but begins to sublime in small needles, below this temperature.

The dinitro-tetramethyl-benzene of Jannasch and Fittig also melts at 205°, and crystallises in colourless rhomboidal crystals, which have not been measured, but tetramethyl-benzene is solid whilst cymene is liquid. The ethyl-xylene of Ernst and Fittig gives a trinitro-derivative fusible at 119°, which would seem to indicate that its dinitro-derivative melts at a much lower temperature.

II. Hydrocarbons soluble in sulphuric acid and recoverable by distillation.

Isoxylene boiling at 139°—140°. Its dinitro-compound crystallises from hot alcohol in very fragile prisms, or by spontaneous evaporation in thin plates of the monoclinic system, fusible at 92°—93°. This is the dinitro-xylene of Fittig.

Pseudocumene, boiling at 165°—167°, gives two dinitro-compounds melting at 86°, one in plates, the other in fine needles.

The *Cymene* of this series is accompanied by naphthalene. It has not been further studied.

W. A. T.

Diphenylbenzene. By G. SCHULTZ (Deut. Chem. Ges. Ber., vi, 415—418).

BY passing benzene through red-hot tubes, Berthelot obtained, besides diphenyl, three other bodies, which he calls chrysene, benzerythrene and bitumen. This chrysene is however a mixture of different bodies, of which two hydrocarbons were isolated. One of them is readily soluble in alcohol, and forms crystals melting at about 85°, and boiling at 360°. The second hydrocarbon is identical with the diphenylbenzene which Riese obtained by acting with sodium on a mixture of monobromobenzene and paradibromobenzene. According to Riese this hydrocarbon is insoluble in boiling alcohol, but this is not correct; although it is but sparingly soluble, it may be recrystallised from an alcoholic solution.

When diphenylbenzene is oxidised with a solution of chromic acid in acetic acid, it yields *paraphenylbenzoic* acid, $C_6H_4\left\{\begin{matrix}C_6H_5\\CO_2H\end{matrix}\right.$, which is isomeric with the acid which Fittig obtained from phenanthrene.

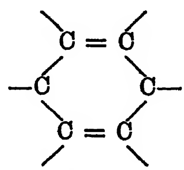
It is sparingly soluble in water, more freely in ether and alcohol, and forms needles melting at 216°—217°, and subliming above this temperature in long needle-shaped crystals.

By further oxidation it is converted into terephthalic acid, and by heating it with quicklime, it is resolved into carbon dioxide and diphenyl.

C. S.

New Conversion of Turpentine into Cymene. By A. Kekulé (Deut. Chem. Ges. Ber., vi, 437).

When turpentine oil is heated in contact with iodine, best in a flask with inverted condenser attached, considerable quantities of a colophene-like polymeride of turpentine are formed, together with a certain amount of cymene (boiling at the normal temperature and of the ordinary odour; also yielding toluic acid of melting-point 176° by oxidation with nitric acid, and terephthalic acid by treatment with chromic acid). The author considers that the iodine unites with the turpentine hydrocarbon, forming a di-iodide, which splits up into cymene and hydriodic acid, as the dibromide does under somewhat similar conditions (Barbier, Oppenheim), and hence gives the following formula as the most probable expression of the structure of the carbon nucleus:—



50 grams of turpentine and 23 of iodine gave 10 of cymene. Free bromine vapour led into heated turpentine gives rise to brominated bodies and polymerides, but forms very little cymene.

C. R. A. W.*

Oxidation-Products of Colophony. By J. Schreder (Deut. Chem. Ges. Ber., vi, 413).

Fused caustic potash does not act on the terpene-resins, but nitric acid oxidises them. Colophony yields a resinous acid, and principally isophthalic acid, besides a large quantity of trimellitic acid.

C. S.

Formation of Stilbene. By B. Radziszewski (Deut. Chem. Ges. Ber., vi, 390).

When a mixture of barium phenylacetate and sulphur is subjected to dry distillation, hydrosulphuric acid and other gases are evolved, and a product passes over, which after pressure and crystallisation from alcohol, and finally from ether, was found to be stilbene, the yield of this substance being so large as to make the above process an advantageous one for preparing it.

* The abstractor has shown (pp. 552, 690, of this volume) that cymene is contained *as such* in oil of turpentine, and may be obtained free from bodies of $C_{10}H_{16}$ formula by treating the oil of turpentine with an agent (such as sulphuric acid), which will polymerize the terpene without acting on the cymene; and has also pointed out that the ease with which the dibromide of a terpene splits up into hydrobromic acid and cymene, varies inversely with the boiling-point of the original terpene.—C. R. A. W.

The author is endeavouring to ascertain which of the following equations represents the reaction :—

$$(1.)\ \left.\begin{matrix} C_6H_5—CH_2—CO_2 \\ C_6H_5—CH_2—CO_2 \end{matrix}\right\} Ba + S_2 = \begin{matrix} C_6H_5—CH \\ \| \\ C_6H_5—CH \end{matrix} + BaSO_4 + H_2S + C_2.$$

$$(2.)\ \left.\begin{matrix} C_6H_5—CH_2—CO_2 \\ C_6H_5—CH_2—CO_2 \end{matrix}\right\} Ba + S = \begin{matrix} C_6H_5—CH \\ \| \\ C_6H_5—CH \end{matrix} + C_2H_2 + BaSO_4.$$

Lead phenylacetate distilled with excess of sulphur yields not only stilbene, but also a hydrocarbon having a lower melting-point.

T. B.

New Members of the Stilbene Group. By J. STRAKOSCH (Deut. Chem. Ges. Ber., vi, 328).

THE action of alcoholic potash on nitrobenzyl chloride was found to give rise to the formation of *dinitrostilbene*. In order to prepare dinitrostilbene, an aqueous solution of potash is added to an alcoholic solution of nitrobenzyl chloride. The dinitro-stilbene then separates in the form of yellow flocks, which can be purified by crystallisation from nitrobenzene.

Laurent obtained a *mixture of mononitro- and dinitro-stilbene* by the action of nitric acid on stilbene, but the latter derivative was not obtained in a pure state.

Dinitrostilbene forms brilliant yellow crystals with a greenish reflection; it is very slightly soluble in alcohol, insoluble in ether and benzene, but nitrobenzene and hot glacial acetic acid dissolve it with tolerable facility. It melts at a temperature above 280°, and sublimes in yellow leaflets. Nitric acid converts it into resinous products.

Nitramidostilbene.—An attempt to prepare amido-stilbene and azo-stilbene by the action of alcoholic potash on dinitro-stilbene did not lead to a satisfactory result, but *nitramidostilbene* was obtained by digesting dinitrostilbene with alcoholic ammonium sulphide, evaporating the product, extracting the residue with strong hydrochloric acid, precipitating the liquor with soda, and washing the precipitate with dilute hydrochloric acid. This substance crystallises from nitrobenzene in purple-red leaflets. It is very slightly soluble in alcohol, ether, or benzene, insoluble in water. When heated to 229—230°, it melts, and at a higher temperature sublimes in red leaflets. Hot hydrochloric acid dissolves it, and on cooling a hydrochloride is deposited in shining yellow needles. This salt is decomposed by water, or by heating, hydrochloric acid being separated. It may be crystallised without change from alcohol containing hydrochloric acid. Analysis showed its composition to be $C_{14}H_{12}N_2O_2,HCl$. An attempt to prepare a double platinum salt was unsuccessful.

Diamidostilbene.—This substance was obtained by heating dinitrostilbene with alcoholic ammonium sulphide to 100° for about half an hour, evaporating the product, extracting the residue with hydrochloric acid, and precipitating the base by means of soda. When

crystallised from dilute alcohol, diamidostilbene forms shining leaflets which become brown on exposure to the air, and dissolve with difficulty in benzene, ether, and water. At 170° it melts and becomes brown, and at a higher temperature sublimes in white leaflets, partial decomposition taking place at the same time. *Amidostilbene hydrochloride* crystallises in large white leaflets; it is easily soluble in water and hot hydrochloric acid, and slightly soluble in alcohol. The *sulphate* forms needles easily soluble in water and dilute sulphuric acid. The nitrate forms yellow granular crystals which dissolve readily in water and alcohol. An amorphous double platinum salt having a dark red colour was obtained. It is insoluble in water, but slightly soluble in hot alcohol.

The author intends to investigate the action of hydriodic acid on dinitrostilbene, and to study the conditions necessary for the transformation of benzyl chloride into stilbene by the action of alcoholic potash.

T. B.

On some Naphthalene Compounds. By J. Grabowski (Deut. Chem. Ges. Ber., vi, 224—225).

A mixture of chloral, sulphuric acid, and naphthalene, if kept cool, soon solidifies, and after removal of the sulphuric acid by washing with water, leaves *dinaphthyltrichlorethane*, $CCl_3CH(C_{10}H_7)_2$, as a white mass. This is tolerably soluble in ether, but with difficulty in alcohol, so that on adding alcohol to its ethereal solution, it crystallises out in thick six-sided tables. On boiling it with alcoholic potash, a molecule of hydrochloric acid is eliminated, and *dinaphthyl-dichlorethylene*, $C_2Cl_2(C_{10}H_7)_2$, is produced. This substance crystallises from hot aniline in yellow nodules which are soluble with difficulty in alcohol or ether, but freely in chloroform, carbonic disulphide, and acetone.

C. E. G.

Benzylnaphthalene. By Ch. Proté (Compt. rend., lxxvi 639).

The author has prepared this hydrocarbon by Zincke's method, namely, by the action of powdered zinc on a mixture of naphthalene and benzyl chloride.

After the completion of the reaction, on submitting the product to distillation, first some unaltered naphthalene and then between 320°—350° an oily liquid passes over, which solidifies in great part in the receiver; it is separated from adherent oil by pressure and crystallised from alcohol.

Benzylnaphthalene, $C_{10}H_7.C_7H_7$, crystallises in colourless needles, which melt at 64°; it is very soluble in ether, but insoluble in water.

H. E. A.

Phenanthrene, a new Hydrocarbon from Coal-tar. By R. FITTIG and E. OSTERMAYER (Ann. Chem. Pharm., clxvi, 361—382).

Phenanthrene, $C_{14}H_{10}$, an isomeride of anthracene, was found in a neutral coal-tar oil boiling between 300°—400°. It was isolated by subjecting the oil to fractional distillation and cooling the portions boiling above 300° to 0°. The crystals were dried on blotting paper and repeatedly crystallised from alcohol to remove anthracene and other bodies. Phenanthrene is sparingly soluble in cold alcohol, but dissolves readily in hot alcohol, ether, benzene, acetic acid, and carbon sulphide. It crystallises in small plates, which in the pure state are brilliant and colourless, but generally have a yellowish colour. It melts at 99°—100°, and very readily sublimes, but boils only at a temperature much above 300°. On mixing cold saturated solutions of the hydrocarbon and picric acid, the compound, $C_{14}H_{10} + C_6H_2(NO_2)_3OH$, separates after some time in red needles melting at 143°. When bromine is added drop by drop to an ethereal solution of phenanthrene, the additive compound, $C_{14}H_{10}Br_2$, is formed, crystallising in four-sided prisms. It is a very unstable body, decomposing spontaneously on keeping.

Phenanthrene-quinone, $C_{14}H_8O_2$, is produced, together with carbon dioxide, by gently heating the hydrocarbon with a mixture of one part of potassium dichromate, $1\frac{1}{2}$ part of sulphuric acid, and 3 parts of water. The quinone is more soluble in alcohol than anthracene (anthraquinone ?), and dissolves readily in benzene and acetic acid, crystallising in tufts of long orange-yellow needles, melting at 198°, and subliming at a higher temperature with partial decomposition to brilliant, transparent orange-red plates. It dissolves in concentrated sulphuric acid without alteration, but on heating the solution, decomposition takes place. When it is heated with bromine in sealed tubes to 100°, a compound is produced which is but very little soluble in all common solvents, and appears to be a dibromo-quinone. Phenanthrene-quinone is not reduced by sulphurous acid in the cold, but by heating it with an aqueous solution to 100° it dissolves, and on cooling almost colourless brilliant needles separate out, consisting probably of the hydroquinone, a very unstable body, which rapidly absorbs oxygen from the air. It is reduced by zinc-dust, yielding again the original hydrocarbon, but the temperature at which this change takes place is higher than that required for the reduction of anthraquinone.

Diphenic acid, $C_{14}H_{10}O_4$, is a product of the oxidation of the quinone, and is always obtained in small quantity in the preparation of the latter. It is most conveniently prepared by heating the impure hydrocarbon containing anthracene with chromic acid solution, and crystallising the mixture of the quinones from alcohol in order to remove an amorphous substance. The quinones are again treated with the oxidising mixture, which does not act on anthraquinone, and extracting the acid from the product by ammonia. Diphenic acid is sparingly soluble in cold water, more freely in hot water, and readily in alcohol and ether; it crystallises on quickly cooling the solution, in shining little plates, but if the solution cools down slowly, it is obtained in transparent compact

prisms containing no water; it separates in the same form on allowing an alcoholic solution to evaporate. By the evaporation of a solution in dilute alcohol, it was once obtained in very large transparent crystals containing two molecules of water. The acid melts at 226°, and sublimes in long transparent needles; when heated above its melting point it blackens and decomposes. It is a strong bibasic acid.

Barium diphenate, $C_{14}H_8O_4Ba + 4H_2O$, is readily soluble in water and forms large transparent crystals. *Calcium diphenate*, $C_{14}H_8O_4Ca + 2\frac{1}{2}H_2O$, is a very soluble salt and does not crystallise well. *Magnesium diphenate*, $C_{14}H_8O_4Mg + 4H_2O$, crystallises in plates. *Silver diphenate*, $C_{14}H_8O_4Ag_2$, is a bulky white precipitate dissolving in a large quantity of hot water.

When the acid is heated with an excess of quicklime, it does not yield diphenyl, as might have been expected, but is converted into *diphenylene ketone*, $C_{13}H_8O$, crystallising from alcohol in large, transparent, pale-yellow plates or thick compact crystals, melting at 83·5°—84° and boiling at above 300°; it volatilises slowly with vapour of water and dissolves in cold concentrated sulphuric acid with a wine-red colour, and is again precipitated by water, but only if the solution has not previously been heated. When diphenylene ketone is introduced into small portions into fused caustic potash it is converted into *phenylbenzoic* acid, $C_{13}H_{10}O_2$, which is almost insoluble in cold water, sparingly soluble in hot water, and very freely in alcohol; from a hot aqueous solution it crystallises in small ramified needles resembling hoar-frost, and melting at 110°—111°. On slowly cooling it solidifies to a crystalline mass, but when rapidly cooled it remains viscid and transparent for days, but becomes crystalline on stirring it with a platinum-wire.

Calcium phenylbenzoate, $(C_{13}H_9O_2)_2Ca + 2H_2O$, is sparingly soluble in water and forms small crystals. When this salt or the acid is heated with quicklime, the ketone is re-generated, but at the same time a small quantity of *diphenyl* is produced, which may be obtained in larger quantity by heating the calcium salt without quicklime. The formation of this hydrocarbon shows that phenylbenzoic acid and diphenic acid have the following constitution:—

Phenylbenzoic acid.	Diphenic acid.
$\begin{array}{l} C_6H_4.CO_2H \\ \vert \\ C_6H_5. \end{array}$	$\begin{array}{l} C_6H_4.CO_2H \\ \vert \\ C_6H_4.CO_2H. \end{array}$

The formation of diphenyl-ketone from diphenic acid is quite analogous to that of dimethyl-ketone from acetic acid:—

$$\begin{array}{l} C_6H_4.CO.OH \\ \vert \\ C_6H_4.CO.OH \end{array} = \begin{array}{l} C_6H_4 \\ \vert \\ C_6H_4 \end{array}\!\!\Big> CO + CO_2 + H_2O.$$

It appears, however, more probable that the molecular formula of the ketone is $C_{26}H_{16}O_2$. Kekulé has lately shown that on heating calcium benzoate a small quantity of anthraquinone is formed, and Jaffé, as well as Barth and Sennhofer, has found that di- and trioxybenzoic

acids are readily converted into derivatives of anthracene. Phenylbenzoic acid behaves in a very similar way, as the following equations show:—

Anthraquinone.

$$\begin{array}{c} C_6H_4H.CO.OH \\ \times \\ C_6H_4H.CO.OH \end{array} = C_6H_4\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle C_6H_4 + 2H_2O.$$

Diphenylene ketone.

$$2\begin{array}{l} C_6H_4.CO.OH \\ | \\ C_6H_5 \end{array} = \begin{array}{l} C_6H_3 \\ | \\ C_6H_5 \end{array}\left\langle\begin{array}{c}CO\\CO\end{array}\right\rangle\begin{array}{l} C_6H_3 \\ | \\ C_6H_5 \end{array} + 2H_2O.$$

Diphenylene ketone would therefore be *diphenyl-anthraquinone;* on fusing it with potash, it again yields phenylbenzoic acid, just as anthraquinone is resolved by this reaction in two molecules of benzoic acid. The oxidation of phenanthrene to diphenic acid shows further that this hydrocarbon must be regarded as a diphenyl in which two atoms of hydrogen are replaced by the "chain" —CH=CH—, and this group yields by oxidation —CO—CO—.* Phenanthrene would therefore have the constitution which Graebe and Liebermann have assigned to anthracene.

C. S.

Phenanthrene. By C. Graebe (Ann. Chem. Pharm., clxvii, 131—166).

In the purification of crude anthracene, a dark, yellowish-brown, crystalline mass is obtained, melting at a few degrees below 100°, and boiling between 310°—360°. From this product phenanthrene may be isolated by distillation and repeated recrystallisation from alcohol. It is preferable, however, first to prepare the picric acid compound by dissolving the crude material and 1⅓ part of picric acid in hot coal-tar naphtha boiling between 100°—140°. The compound, $C_{14}H_{10} + C_6H_2(NO_2)_3OH$, then crystallises out on cooling in long, golden-yellow, or reddish-yellow prisms, melting at 145°. The same compound is obtained in fine needles by mixing cold saturated alcoholic solutions of phenanthrene and picric acid. It may be boiled with a large excess of alcohol without decomposition. Water resolves it slowly, and alkalis quickly into its two constituents.

Phenanthrene, $C_{14}H_{10}$, is readily soluble in ether, benzene, and carbon sulphide; it dissolves also freely in boiling alcohol, but sparingly in cold alcohol, and crystallises in colourless plates, which, when quite pure, exhibit a blue fluorescence, but in a less marked degree than anthracene. It melts at 100°, and boils at 340°, the whole column of mercury being in the vapour.

* The authors believe that all quinones contain the group —CO—CO—, and not, as Graebe assumes, the group O—O. The same view is held by Petersen (*Deut. Chem. Ges. Ber.*, vi, 400), who also supposes that in ordinary quinone the two oxygen-atoms occupy the positions 1 : 4.

Phenanthrene-quinone, $C_{14}H_8(O_2)''$, is readily formed by dissolving the hydrocarbon in hot glacial acetic acid, and adding a solution of chromic acid in acetic acid so gradually that the liquid is just kept at the boiling point; to finish the reaction the solution must be boiled for some time. On distilling off the greater part of the acetic acid and adding water to the residue, a crystalline precipitate of the quinone is obtained. It is easily purified by crystallising it from glacial acetic acid, but more conveniently by dissolving it in a solution of acid sodium sulphite, and reprecipitating it with an acid.

Phenanthrene-quinone is almost insoluble in cold water, and dissolves but sparingly in hot water and in cold alcohol; it is a little more freely soluble in boiling alcohol, and still more so in ether, benzene, and glacial acetic acid. It crystallises in dark reddish-yellow prisms. Like other quinones, it is reduced by zinc-dust to phenanthrene; it dissolves in cold sulphuric acid, but even at 100° no sulphonic acid is formed, but on heating the solution more strongly, decomposition takes place. It may, however, be converted into sulphonic acids by acting on it with sulphur trioxide. Concentrated nitric acid dissolves it with a red colour, and on adding water, the quinone is reprecipitated. A boiling mixture of sulphuric acid and nitric acid converts it, but not readily, into nitro-compounds, from which, by crystallisation from acetic acid, *dinitrophenanthrene-quinone*, $C_{14}H_6O_2(NO_2)_2$, was obtained in yellow, silky plates.

On heating phenanthrene-quinone with soda-lime, it yields *diphenyl*, carbon dioxide, and hydrogen:—

$$C_{14}H_8O_2 + 4NaOH = C_{12}H_{10} + 2Na_2CO_3 + H_2.$$

Anthraquinone yields with soda-lime chiefly benzene; these reactions show that two aromatic nuclei are linked together directly in phenanthrene, but not in anthracene.

Phenanthrene-hydroquinone, $C_{14}H_8(OH_2)$. While anthraquinone is not acted on at all by sulphurous acid, phenanthrenequinone is reduced by it, slowly, even in the cold. On heating the quinone with an excess of aqueous sulphurous acid to 100°, it dissolves, and, on cooling, the hydroquinone crystallises in long, colourless needles. An alcoholic solution of sulphur dioxide reduces the quinone still more readily. Phenanthrene-hydroquinone absorbs oxygen in the moist state, but when dry it is more stable. By boiling it with water in presence of air, it is first converted into a brownish-black quinhydrone, and then into the quinone. The same reaction takes place when it is acted on by ferric chloride, nitric acid, chromic acid, &c.

When the hydroquinone is dissolved in caustic potash, and the solution exposed to the air, a green precipitate is formed, which gradually changes into the quinone. This body is coloured brown by acids, and green again by alkalis; it consists probably of the potassium salt of phenanthrene-quinhydrone, and is also formed by dissolving phenanthrene-quinone in ammonium or potassium sulphide, or in caustic soda with the aid of zinc-dust, and exposing these solutions to the air.

Diacetyl-phenanthrenehydroquinone, $C_{14}H_8O_2(C_2H_3O)_2$, is produced by heating the hydroquinone with acetic anhydride to 140°—150°. It crystallises from hot benzene in colourless plates melting at 202°.

This body is a very stable compound, which is not oxidised by boiling it with a solution of potassium dichromate and sulphuric acid, but a solution of chromic acid and acetic acid converts it into the quinone. Heated with caustic potash of spec. grav. 1·3, it is not changed, but on concentrating the liquid, decomposition takes place, and on adding water, the green body already mentioned is precipitated.

Phenanthrenequinone-sodium sulphite, $C_{14}H_8O_2.NaHSO_3 + 2H_2O$, is produced by dissolving the quinone in a warm solution of acid sodium sulphite; it crystallises in small colourless plates. It is slowly decomposed by water, quickly by acids and alkalis; when exposed to the air it absorbs oxygen, and sulphuric acid is formed.

Phenanthrenequinone-potassium sulphite is a very similar body. The constitution of these bodies is most probably the following:—

$$C_{14}H_8\begin{cases} OH \\ OSO_3Na. \end{cases}$$

By means of these compounds, the presence of phenanthrene can be easily ascertained in crude anthracene, namely, by oxidising that substance with acetic acid and chromic acid, treating the product with sodium carbonate to remove acids, and heating the insoluble portion with a solution of acid sodium sulphite. This reagent dissolves only phenanthrenequinone, which may be reprecipitated by an acid, and easily recognised by its properties.

Phenanthrenesulphonic acid, $C_{14}H_9\ SO_3H$, is produced, together with some disulphonic acid, by heating phenanthrene with sulphuric acid to 100°, preparing the lead-salt, and decomposing it with hydrogen sulphide. It is a crystalline mass, more freely soluble in hot than in cold water. $(C_{14}H_9SO_3)_2Ca + 4H_2O$ crystallises in small plates, and dissolves readily in alcohol and hot water. $(C_{14}H_9SO_3)_2Pb + 2H_2O$ is freely soluble in water and alcohol, and does not crystallise well. The barium-salt has similar properties.

Reduction of Phenanthrene.—Phenanthrene not reduced by sodium-amalgam in alcoholic solution, but by heating it with phosphorus and hydriodic acid to 200°, it is converted into *tetrahydro-phenanthrene*, $C_{14}H_{14}$, a liquid boiling at 300°—310°, whilst at 240° the hydrocarbon $C_{14}H_{18}$ is formed, which is also a liquid, and boils below 300°.

Nitro-compounds.—Cold concentrated nitric acid converts phenanthrene into the mononitro-compound, which, by dissolving it in acetic acid, and adding water, is obtained as a yellow crystalline precipitate, melting between 70°—80°. If the nitric acid be not kept cold, some dinitro-compound is formed, which may be obtained in quantity by heating to 100°; from acetic acid it separates in yellow crystals, melting between 150°—160°.

Synthesis of Phenanthrene.—Phenanthrene is formed, together with toluene, by passing stilbene through a red-hot tube:—

$$(1.)\quad \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} = \begin{array}{c} C_6H_4.CH \\ |\qquad\| \\ C_6H_4.CH \end{array} + H_2.$$

$$(2.)\quad \begin{array}{c} C_6H_5.CH \\ \| \\ C_6H_5.CH \end{array} + 2H_2 = 2C_6H_5.CH_3.$$

Phenanthrene is also formed by the same reaction from dibenzyl, which, as Dreher and Otto have shown, is first converted into toluene and stilbene. From these reactions it appears probable that phenanthrene has the constitution which has hitherto been assigned to anthracene.

Constitution of Quinone.—Fittig regards the quinones as double acetones (p. 894 of this volume). Some of the reactions of these bodies are perhaps more simply explained by this hypothesis, but all the facts taken together make it much more probable that the quinones have the constitution first assigned to them by the author.

If quinones contained the group CO twice, they would belong to the additive products, and would therefore be less stable than the hydroquinones, but just the opposite is the case. Acetones form secondary alcohols by taking up two atoms of hydrogen for each atom of oxygen, but quinones take up only one atom of hydrogen for one of oxygen. Further, in acetones each atom of oxygen may be replaced by two of chlorine, whilst in quinones two of chlorine always replace two atoms of oxygens. Quinones are formed by replacing two atoms of hydrogen by two of oxygen, whereas acetones are produced by replacing two of hydrogen by only one atom of oxygen.

These reactions can only be explained by assuming that quinones contain the dyad group, O—O.

C. S.

Phenanthrene. By H. LIMPRICHT
(Deut. Chem. Ges. Ber., vi, 532—533).

THIS hydrocarbon is readily soluble in cold alcohol, and may, therefore be separated from anthracene and other hydrocarbons by boiling the crude product with alcohol. The cold solution is filtered, the alcohol distilled off, and the residue subjected to the same treatment until the hydrocarbon melts at about 100°. It is purified by converting it into the picric acid compound, which is recrystallised from hot alcohol and then decomposed by ammonia. To obtain it quite pure it is heated with a little acetic acid and potassium chromate on a water-bath, and recrystallised from alcohol.

It forms rather large plates melting at 96°, and beginning to sublime at 100°; it is readily soluble in alcohol, ether, acetic acid, and benzene, the solutions exhibiting a fine blue fluorescence. The picric acid compound, $C_{14}H_{10} . C_6H_2(NO_2)_3OH$, forms yellow needles melting at 143°, but if the hydrocarbon was not pure, they have a red colour.

Phenanthrene dibromide, $C_{14}H_{10}Br_2$, is produced by mixing well-cooled solutions of phenanthrene and bromine in carbon sulphide. It forms well-defined, four-sided prisms, which even in closed vessels gradually undergo spontaneous decomposition; it melts at 98° with loss of hydrobromic acid, *monobromophenanthrene*, $C_{14}H_9Br$, being formed, which is also produced by boiling the dibromide with alcohol or water. This compound forms thin white prisms melting at 63°, and subliming without decomposition. On adding bromine to its solution in carbon sulphide, it is converted into *dibromophenanthrene*, $C_{14}H_8Br_2$, crystallising in white, warty needles; on heating the solution with bromine,

tribromophenanthrene, $C_{14}H_7Br_3$, is obtained in silky needles melting at 126°.

The mother-liquor of the dibromide contains an oily monobromophenanthrene which is soluble in cold ether, and an insoluble *dibromophenanthrene*, which is a yellowish crystalline powder melting at 202°.

Phenanthrene-quinone was formed by heating the hydrocarbon with acetic acid and chromic trioxide; it crystallises in yellowish-red needles melting at 202°. On heating it with water and bromine to 180°, it yields $C_{14}H_6Br_2O_2$ in yellow, warty crystals melting at 230°. In the preparation of the quinone, a bye-product is formed, separating from alcohol as a red oil having probably the composition $C_{14}H_{10}O_2$, and yielding by oxidation with chromic trioxide an isomeric quinone, $C_{14}H_8O_2$, which separates from alcohol in granular crystals melting at 156°.

C. S.

Cresol Derivatives. By R. Biedermann (Deut. Chem. Ges. Ber., vi, 325).

When cresol in the state of vapour is treated with chlorine, abundance of hydrochloric acid is evolved, and the liquid becomes brown. The hydrochloric acid may be now removed by a current of carbonic anhydride, after which a portion boiling between 235°—245°, may be separated by fractionation. This, when cooled in a freezing mixture, deposits crystals having the composition of *monochlorocresol*. It melts at 56°, boils at about 240°, and is easily soluble in alcohol, ether, chloroform, benzene, or petroleum. Monochlorocresol was treated with ammonia, aniline, potassium cyanide, and silver cyanide, but the products were not of such a nature as to invite further research. No orcin was obtained either by heating it with alcoholic potash, or by fusing it with potassium hydrate. These results tend to show that the atom of chlorine is in the benzene nucleus and not in the side-chain.

Cresol-sulphonic acid was prepared by heating sulphuric acid and the above-mentioned cresol to 60°. The barium salt and calcium salt are very soluble, crystallise badly, and have a tendency to form basic salts. The potassium salt forms star-shaped groups containing two molecules of water. The salts of this acid appear to correspond with those of the γ-cresol-sulphuric acid of Engelhardt and Latschinoff. On fusing the potassium salt with potash and treating the product in the usual way, pyrocatechin was obtained, but no orcin.

With the view of obtaining orcin, the author treated cresol with an alkaline solution of iodic acid and iodine, according to the method of Körner, and thus obtained an iodised cresol in the form of an oil which decomposed below its boiling point, and when this oil was heated to 250°—300° with alcoholic potash, it was decomposed, a brown amorphous mass being obtained. This substance was several times dissolved in an alkali and precipitated by an acid, and was afterwards purified by various solvents. It becomes red on treatment with ammonia, dissolves in alkalis with a dark red colour, softens at 50°, melts at 100°, and is free from iodine.

Analysis led to the formula—

$$\begin{matrix} C_6H_3 \left\{ \begin{matrix} CH_3 \\ OH \\ O \end{matrix} \right. \\ C_6H_3 \left\{ \begin{matrix} OH \\ CH_3. \end{matrix} \right. \end{matrix}$$

This substance yields a nitro-derivative which is still under investigation.

T. B.

Phenyl-propyl Alcohol. By R. Fittig (Deut. Chem. Ges. Ber., vi, 214—216).

In conjunction with Krügener the author has already studied the action of sodium amalgam on a warm aqueous solution of cinnamic alcohol, and allylbenzene was found among the products of the reaction. The investigation of this subject has been continued by Bügheimer, who finds that an alcohol boiling at 234°—235° is also formed. This alcohol has the composition $C_9H_{12}O$, and when oxidised with chromic anhydride, yields hydrocinnamic acid. The author considers that allylbenzene is formed by the replacement of the hydroxyl of cinnamic acid by hydrogen:

$$C_6H_5—CH=CH-CH_2OH + H_2 = C_6H_5-CH=CH-CH_3 + H_2O.$$

If this supposition be correct, the allylbenzene thus produced should have a different constitution from an allylbenzene obtained by the direct attachment of allyl to benzene. All the author's endeavours to obtain an allylbenzene directly from benzene have failed.

Bügheimer has found that the commercial cinnamic alcohol obtained by distillation of storax, contains a considerable proportion of phenyl-propyl alcohol, and it is highly probable that the styrocone of Scharling consisted principally of phenyl-propyl alcohol.

Bügheimer is engaged in the further study of allylbenzene and phenyl-propyl alcohol.

T. B.

On Brasilin and Resorcin. By E. Kopp (Deut. Chem. Ges. Ber., vi, 446).

In the manufacture of Brazil-wood extract, a considerable quantity of a crust is obtained, containing much brasilin and lime-brasilin lake; this is treated with 5 per cent. hydrochloric acid, and boiled with water containing 10—15 per cent. of alcohol, brasilin then crystallising out of the liquor on cooling. The wash- and mother-waters, &c., evaporated to dryness with chalk, furnish resorcin on dry distillation.

Brasilin when pure is colourless and dissolves to a colourless liquid in recently boiled water; dilute alkalis dissolve it, the solution becoming instantly more or less carmine-coloured; when heated with zinc dust in a closed vessel on the water-bath, the carmine-coloured liquid is decolorised, forming a most sensitive reagent for free oxygen. The

resorcin obtained by the dry distillation of brasilin, even when impure, is of good quality, this mode of preparation being the simplest, easiest, and least costly of any yet proposed; the crystals of resorcin melt at 98°—99°, and distil at 266°—267°. A characteristic reaction for resorcin is to treat a minute quantity with fuming sulphuric acid, which dissolves it with an orange-yellow colour, gradually darkening and passing into greenish blue and a beautiful blue in 20—30 minutes; if warmed to 90°—100°, this blue liquid becomes of a fine purple red.

Anhydrous brasilin is expressed by the formula $C_{22}H_{18}O_7$; its relation to hæmatoxylin is indicated by the equation—

$$\underset{\text{Brasilin.}}{C_{22}H_{18}O_7} + H_2O = \underset{\text{Hæmatoxylin.}}{C_{16}H_{14}O_6} + \underset{\text{Resorcin.}}{C_6H_6O_2}.$$

C. R. A. W.

Methyl-Alizarin and Ethyl-Alizarin. By E. Schunck (Chem. News, xxvii, 171).

The results of the author's analyses of the yellow colouring matter accompanying artificial alizarin (anthraflavic acid), led to the formula, $C_{15}H_{10}O_4$: hence he was induced to view it as a body homologous with alizarin. The more recent analyses of Perkin imply that it is isomeric with alizarin, while Græbe and Liebermann assign to it the formula, $C_{14}H_8O_3$, and consider it to be monoxanthraquinone. With the hope of throwing further light upon the constitution of this substance, the author undertook the study of some of the substituted derivatives of alizarin.

Artificial alizarin was treated with a mixture of methyl iodide, caustic potash, and a little methyl alcohol in closed tubes, at a moderate temperature. The contents of the tubes were subsequently evaporated to dryness, and the residue treated successively with water, alcohol, and dilute caustic potash. The second residue, which was found to consist mainly of the potassium compound of methyl-alizarin, was treated with hydrochloric acid, and the insoluble orange-coloured flocks dissolved in boiling alcohol. The alcohol, on cooling, deposited crystalline needles of methyl-alizarin.

Ethyl-alizarin was prepared in a similar manner.

Methyl-alizarin crystallises in long reddish-yellow needles, which are almost insoluble in boiling water, but readily soluble in oil of vitriol.

It volatilises entirely by heat, yielding a sublimate of lustrous yellow scales. It is not decomposed by solution of caustic potash, but when carefully fused with that alkali, it is reconverted into alizarin. It differs essentially from alizarin in the appearance of the spectrum of its alkaline solution, and in the fact that it will not dye mordanted cloth; while it somewhat resembles anthraflavic acid, not only in the points just mentioned, but also in the fact that both substances yield crystallisable sodium and potassium compounds.

If the formula of methyl-alizarin be $C_{14}H_6(OH)(OCH_3)O_2$, that of the potassium-compound would be $C_{14}H_6(OK)(OCH_3)O_2$, and it would contain 13·3 per cent. of potassium. A specimen of the latter salt

dried at 130° was found to contain 12·6 per cent. of potassium. It would appear, therefore, that the constitution of methyl-alizarin is analogous to that of the diacetyl-alizarin prepared by Perkin.

J. W.

A New Method of Obtaining Ketones. By C. ENGLER and A. LEIST (Deut. Chem. Ges. Ber., vi, 257—259).

BY treating 100 grams of pure cinnamic aldehyde with sodium, a crystalline compound is formed which on heating with an equal weight of methyl iodide in sealed tubes to 120°—130°, gave 5 grams of *aceto-cinnamone*, the chief product consisting of a beautiful red colouring matter, belonging undoubtedly to the class of Baeyer's phenol-colours. The same ketone is formed, but also in small quantity only, when cinnamic aldehyde and methyl iodide are boiled with zinc chloride or phosphorus pentoxide.

By subjecting a mixture of benzaldehyde and phenol to the same reaction, no benzophenone was formed, whereas methyl alcohol and benz-aldehyde gave a small quantity of acetophenone and much colouring matter. Neither acetophenone nor acetocinnamone combines with the acid sulphites of the alkali-metals.

C. S.

On Aceto-cinnamone and other Products of the Dry Distillation of Cinnamate and Acetate of Calcium. By C. ENGLER and A. LEIST (Deut. Chem. Ges. Ber., vi, 254—256).

WHEN an intimate mixture of equal numbers of molecules of calcium cinnamate and acetate is submitted to dry distillation, an oily distillate is obtained which may be separated by fractional distillation into a number of bodies.

Acetocinnamone, $C_6H_5—CH=CH—CO—CH_3$, is obtained by repeated fractional distillation of that portion of the crude distillate which boils between 220° and 270°. Freshly prepared, it forms a slightly yellow oily liquid of agreeable odour, turning darker when kept. Its sp. gr. is 1·008, and its boiling-point 240°—241°.

The portion of the crude distillate boiling below 220°, contains a considerable quantity of benzene, some toluene, a hydrocarbon boiling at 119° and having the formula, C_5H_6 or $C_{10}H_{12}$, and a quantity of styrol agreeing exactly in properties with that obtained from storax.

The crude distillate boiling between 290° and 330°, deposits on standing, tabular crystals of a body having the formula C_nH_n, which the authors believe to be a *polystyrol*. It melts at 117° and distils undecomposed. The same hydrocarbon is formed in larger quantity when calcium cinnamate is distilled *per se*.

J. R.

Synthesis of Aromatic Acids. By W. WEITH (Deut. Chem. Ges. Ber., vi, 418—422).

THE author has already shown that by heating phenylic mustard-oil (phenyl-sulphocarbimide) with copper-dust, the sulphur is removed,

and phenyl-carbamine is formed, which, however, at the high temperature is converted into benzonitrile.

The author and Merz have further shown that when sulphocarbanilide is heated, it is resolved into aniline and phenyl-sulphocarbimide. Therefore, when sulphocarbanilide is quickly heated with copper-dust, some benzonitrile is produced, but the yield is small.

The mustard-oil from *pseudotoluidine* (orthotolyl-sulphocarbimide) when treated with copper-dust, yields orthotoluonitrile, a limpid and very refractive liquid, smelling like nitrobenzene and boiling at 203°—204.° On heating it with concentrated hydrochloric acid for some hours to 200°, it is converted into orthotoluic acid. When the nitrile is heated with alcoholic potash for 3—4 hours to 130°, it is converted into *orthotoluylamide*, $C_6H_4(CH_3)CONH_2$, crystallising from boiling water in silky, slender, very long needles, melting at 138°.

When solid toluidine is treated with carbon sulphide, it yields a sulphocarbotoluide, which when heated with dilute sulphuric acid, is resolved into toluidine and the corresponding mustard-oil. The latter gives with copper-dust, *paratoluonitrile*, but the yield is small. A better result was obtained by distilling paratolylsulphocarbamide with finely divided copper. Paratoluonitrile forms fine white needles, smelling like benzaldehyde and melting at about 30°. By heating it with hydrochloric acid to 200°, it yields pure paratoluic acid. The action of heat in presence of copper on sulphocarboparatoluide takes place according to the following equations:—

$$CS\begin{cases} NH-C_7H_7 \\ NH-C_7H_7 \end{cases} = CS{=}N-C_7H_7 + C_7H_7NH_2.$$

$$CS{=}N-C_7H_7 + 2Cu = Cu_2S + CN - C_7H_7.$$

$$C\begin{cases} N''' \\ C_7H_7 \end{cases} = N^{v}\begin{cases} C \\ C_7H_7. \end{cases}$$

C. S.

On Crystallised Benzoic Acid from Gum Benzoin.

By P. Grichard (Bull. Soc. Chim. [2], xix, 317).

The author having left a quantity of benzoin macerating with carbon sulphide for a considerable time, found it covered with colourless crystals of benzoic acid, and the carbon sulphide on evaporation yielded a further crop of nearly pure crystals. This solvent might therefore be used to extract benzoic acid from benzoin.

C. E. G.

On Rosolic Acid. By M. Prud'homme (Bull. Soc. Chim. [2], xix, 359, 360).

Fresenius attributes the formation of rosolic acid, on heating a mixture of oxalic acid and phenol with sulphuric acid, to the action of nascent carbonic oxide on sulphophenic acid; but the author believes that the presence of a conjugate phenol-acid is not essential, the sulphuric acid acting merely as a dehydrant. In fact, on replacing the

sulphuric acid by boric, arsenious, or arsenic acid, or even on heating a mixture of phenol and dehydrated oxalic acid, rosolic acid is formed: moreover, the colouring matter is not produced on heating a mixture of crystallised oxalic acid and phenol. The author infers from these results that rosolic acid is a product of the direct action of nascent carbonic oxide on phenol, and that its constitution is correctly expressed by the formula $C_6H_4.COH.OH$, suggested by Kolbe.

C. E. G.

Orthonitrophenolsulphonic Acid, Amidophenolsulphonic Acids, and a new Nitrophenol. By J. POST (Deut. Chem. Ges. Ber., vi, 395).

THE calcium salt of the nitrophenolsulphonic acid obtained from orthonitrophenol is represented by Koerner as containing one molecule of water, whilst the author found $2\frac{1}{2}$ H_2O. New experiments confirmed the author's former results, he having found that the temperature employed by Koerner (170°) is insufficient to expel the whole of the water from the salt. The properties of the calcium salt and the lead salt are still under investigation.

In preparing orthonitrophenolsulphonic acid, it is advantageous to avoid a rise of temperature, and to employ a considerable excess of sulphuric acid. The product is diluted with water, neutralised by marble, and the filtered solution is precipitated with barium chloride. The precipitate, when decomposed by sulphuric acid, yields the orthonitrophenolsulphonic acid.

By nitrating potassium metaphenolsulphonate, an acid was obtained which appears to be identical with orthonitrophenolsulphonic acid.

When Armstrong chlorinated an aqueous solution of the nitrophenolsulphonic acid prepared from nitrophenol melting at 45°, he found that the results were different from those obtained when an alcoholic solution is chlorinated, and the author announces his intention of extending this investigation to orthonitrophenolsulphonic acid.

Orthoamidophenol sulphonic acid may be obtained in small cubes or snow-white needles soluble in 2,800 parts of cold water, by the action of tin and hydrochloric acid on orthonitrophenolsulphonic acid, or by the action of sulphuric acid on orthoamidophenol. These two products appear to be identical, each containing 8·42 per cent. of water. The two amidophenolsulphonic acids obtained by similar methods from nitrophenol melting at 45° appear also to be identical with each other, but differ from those just described. They form nearly colourless highly refractive cubes, which become reddish on recrystallisation. They contain 4·50 per cent. of water ($\frac{1}{2}$ molecule).

In order to decide the identity or non-identity of the above acids, the author proposes to determine accurately their solubility in water.

When phenol is nitrated, a small quantity of an oil is produced, which passes over with the last portions of the 45° nitrophenol. Treatment with hot water removes the 45° compound, and by converting the oil into a potassium salt, decomposing this with sulphuric acid, distilling with water, and again treating with potash, the potas-

sium salt of a new mononitrophenol was obtained in cinnabar-red needles containing half a molecule of water. The new nitrophenol melts between $-7°$ and $2°$.

The author hopes that the nitration of phenol dissolved in acetic acid will give rise to the formation of a proportion of the new compound larger than that which is obtained by the ordinary method.

T. B.

Cresotic Acid. By Biedermann and Pike (Deut. Chem. Ges. Ber., vi, 323).

Cresotic acid was prepared by Kolbe's method from coal-tar cresol boiling at about 203°, and it was observed that only a small portion of the cresol was converted into the acid, one modification of cresol being probably attacked more readily than the others.

The melting point of pure cresotic acid was found to be 174°. It crystallises from water in beautiful shining needles resembling salicylic acid, and strikes a deep violet colour with ferric chloride. The calcium salt and barium salt are very soluble in water, crystallise badly, and retain no water of crystallisation. The silver salt forms a white powder soluble in hot water, and yields *methyl cresotate* when it is heated with methyl iodide. This ether boils at 236°—237°, and smells like gaultheria oil. Alkalis act on it, forming an alkaline methylcresotate, which by further treatment with alkali splits up into methylic alcohol and cresotic acid. Ammonia converts it into methyl alcohol and cresotamide, a solid slightly soluble mass, which has not yet been investigated.

An attempt to prepare the aldehyde of cresotic acid by the distillation of calcium cresotate and calcium formate was unsuccessful, cresol and other products not yet investigated being formed. Nothing giving a crystalline product with sodium bisulphite was obtained.

T. B.

On Igasuric Acid. By H. Ludwig (Arch. Pharm. [3], ii, 137—138).

An examination of this body has led the author to conclude that it belongs to the class of iron-greening tannins.

The acid was prepared by precipitating an aqueous solution of the alcoholic extract of St. Ignatius' beans with neutral acetate of lead, decomposing the precipitate with hydrogen sulphide, and concentrating the filtrate. It formed a yellowish-brown amorphous mass, the solution of which had a strongly acid reaction and a sour astringent taste, and could not be made to crystallise.

The acid did not affect ferrous salts, but caused a dark-green coloration in ferric salts. It rapidly reduced ammoniacal silver-solution, and gave a yellow precipitate with neutral acetate of lead. When neutralised with lime-water, it formed an amorphous greenish-brown lime-salt, which was coloured deep brown by caustic soda, and gave with ferric chloride a green coloration, changing to violet-brown on addition of sodium carbonate.

All these reactions point to the conclusion mentioned above. But the acid did not yield sugar when boiled with dilute sulphuric acid; and the crystalline acid sublimate obtained by heating the lime-salt did not exhibit the characteristic reactions of pyrogallic acid either with ferric chloride or alkalis.*

J. R.

On some Constituents of White Hellebore-root.

By HERMANN WEPPEN (Arch. Pharm. [3], ii, 101—124).

THE author has obtained from this root a bitter substance which he calls *veratramarin*. It exists in aqueous extracts of the root after the separation of the alkaloids, imparting thereto its bitter taste. It was obtained thus:—The sliced root was macerated with cold lime-water, the infusion was freed from lime by means of carbonic acid, and the filtered liquid was mixed with excess of neutral lead acetate and again filtered. The bitter-tasting liquid thus obtained, on standing for some days, deposited on the sides of the vessel a brown crystalline crust (see below). The liquid decanted from this deposit was precipitated with a slight excess of basic lead acetate; the precipitate containing the whole of the bitter substance was decomposed, after thorough washing, by hydrogen sulphide; the filtered liquid was boiled to expel excess of the gas and after cooling mixed with solution of tannin. The precipitate thereby produced was washed, mixed with lead hydrate, evaporated to dryness over the water-bath, and then exhausted with 40 p. c. alcohol. The pale yellow body left on distilling off the alcohol, when dried over sulphuric acid, proved to be too small in quantity to admit of full investigation. It appears to be extremely unstable and probably undergoes decomposition during preparation. It reduces alkaline solutions of copper after boiling with acids but not before, and hence appears to be a glucoside. It is soluble in water but insoluble in ether, benzene, and chloroform, which circumstance makes it difficult to isolate. It is very hygroscopic, deliquescing in the air in a few minutes and rapidly turning dark-brown.

The crystalline body referred to above, which on examination was found to be a lead-salt, was suspended in water and decomposed by hydrogen sulphide; the acid liquid, filtered hot, was evaporated, leaving a mass of crystals which, after purification, formed a white, light crystalline powder not obtainable in large crystals. This body is named by the author *jervic acid*. It is soluble in 10 parts of hot and 100 parts of cold water, sparingly soluble in alcohol and ether, insoluble in benzene, carbon disulphide, chloroform, amyl alcohol, and dilute acids. It gives with neutral and basic lead acetates, precipitates, insoluble in acetic but soluble in nitric and hydrochloric acids; with silver nitrate a white precipitate, soluble in ammonia and unaltered by exposure to light; with mercurous nitrate a brilliant white crystalline precipitate, insoluble in water but soluble in nitric acid. With baryta- and lime-water it gives white precipitates, which turn yellow after

* The author appears to have overlooked the fact that the iron-greening tannins are generally not glucosides, and that they yield by dry distillation oxyphenic, not pyrogallic acid.—J. R.

some time. The formula of jervic acid, as deduced from the author's analyses, is $C_{14}H_{10}O_{12} + 2H_2O$.

J. R.

Salts of Jervic Acid. By H. WEPPEN (Arch. Pharm. [3], ii, 193—210).

THE potassium and sodium salts were obtained by neutralising an aqueous solution of the acid with the pure carbonates and evaporating over sulphuric acid. They are both very soluble in water and have an alkaline reaction.

The barium salt is a heavy, glittering crystalline powder, consisting of six-sided tables. The strontium salt is a crystalline powder, rather more soluble than the barium salt.

Calcium jervate crystallises more distinctly in four- or six-sided rhombic prisms. There are two silver salts, both obtained by precipitation; also a mercurous salt in the form of a crystalline powder.

These salts have all been analysed, with results represented by the following formulæ:—

Potassium jervate	$C_{14}H_6O_{12}K_4.2H_2O$.
Sodium „	$C_{14}H_6O_{12}Na_4.3H_3O$.
Barium „	$C_{14}H_6O_{12}Ba_2$.
Strontium „	$C_{14}H_6O_{12}Sr_2.H_2O$.
Calcium „	$C_{14}H_6O_{12}Ca_2.6H_2O$.
Acid silver „	$C_{14}H_8O_{12}Ag_2.2H_2O$.
Neutral silver „	$C_{14}H_6O_{12}Ag_4$.
Mercurous „	$C_{14}H_6O_{12}Hg_4.4H_2O$.

The author represents jervic acid as tetrabasic. Alkalis colour it yellow, and by boiling it with baryta water a crystallisable acid is produced, upon the investigation of which the author is now engaged.

W. A. T.

Derivatives of Salicylic Acid. By R. WANSTRAT (Deut. Chem. Ges. Ber., vi, 336).

WHEN phosphorous trichloride is allowed to drop into a mixture of aniline and salicylic acid, hydrochloric acid is evolved, and the temperature of the mixture rises to about 180°; when cold the product forms a yellowish brittle mass, which was boiled with water to remove phosphorous acid, hydrochloric acid, and aniline hydrochloride, and the residue was first crystallised from alcohol, animal charcoal being added, and it was finally crystallised several times from water. The substance thus obtained formed small white prisms, having the composition—

$$\begin{array}{l} C_6H_4.OH \\ | \\ CO(NH.C_6H_5). \end{array}$$

The author calls this substance *anilide of salicylic acid*, the term salicylanilide being already engaged. It melts at 134°—135°, is not

attacked by dilute acids, but dilute alkalis cause it to split up into aniline and salicylic acid. When fused with barium hydrate it yields phenol and aniline. It is soluble in sulphuric acid, water reprecipitating it from this solution, and its alcoholic solution strikes a violet colour with ferric chloride.

Nitranilide of salicylic acid, $C_6H_4.OH$

$|$

$CO(NH.C_6H_4NO_2)$. This substance was obtained by a method precisely analogous to that employed in the previous case. When crystallised from alcohol it forms groups of needles which melt at 217°—218°; with acids, alkalis, and ferric chloride, it reacts like the body just described.

Toluidide of salicylic acid, $C_6H_4.OH$

$|$

$CO(NH.C_6H_4CH_3)$. This substance was obtained by the action of phosphorus trichloride on a mixture of toluidine and salicylic acid; it is not easy to prepare, as secondary products are formed to a considerable extent. It crystallises in white prisms melting at 155°—156°, and when boiled with aqueous potash splits up into toluidine and salicylic acid. On fusion with barium hydrate it yields phenol and toluidine. It is far less soluble in water than the anilide of salicylic acid, but with respect to other solvents it behaves like that substance.

T. B.

Derivatives of Salicylic Aldehyde. By W. Haarmann (Deut. Chem. Ges. Ber., vi, 338).

Monobromosalicylanilide.—Equal volumes of aniline and salicylic aldehyde are heated together, and the solid mass obtained on cooling the product is crystallised from alcohol. The new substance forms brick-red shining crystals resembling those of salicylanilide. Analysis led to the formula $C_{13}H_{10}BrNO$.

Salicylanilide hydrocyanate, $\left.\begin{matrix} C_7H_6O \\ C_6H_5 \end{matrix}\right\} N.HCN$, was formed by treating an alcoholic solution of salicylanilide with anhydrous hydrocyanic acid, or by the action of anhydrous hydrocyanic acid on a mixture of aniline and salicylic aldehyde. It forms white leaflets insoluble in water, but easily soluble in alcohol or ether. When exposed to the air the crystals become red; and when they are heated to 100°, hydrocyanic acid is given off and a resinous substance remains.

Salicyl-paranitranilide is formed by the action of paranitraniline on salicylic aldehyde. It crystallises in bright yellow needles, melting at 115°, and behaving in most respects like salicylanilide.

When a mixture of nitraniline and salicylic aldehyde is treated with excess of anhydrous hydrocyanic acid, and the whole is kept in a closed vessel for some days, the mass becomes black, and small red crystals form in it. This red substance was separated by means of alcohol, and was found to melt at 205° and to be insoluble in water, but slightly soluble in hot alcohol or ether. It is decomposed by strong alkalis, with separation of hydrocyanic acid.

Action of Ammonia and Hydrocyanic Acid on Salicylic Aldehyde.—The bottom of a wide-necked flask was covered with a layer of pure ammonium cyanide, and a small open vessel containing salicylic aldehyde was introduced into the flask. The sides of this vessel soon became covered with white crusts, which after some time turned yellow and finally red. This substance when crystallised from alcohol forms red needle-shaped crystals having the composition $C_{29}H_{2},N_{3}O_{3}$. It is insoluble in water, but moderately soluble in alcohol, ether, and cold potash-solution. Concentrated acids or alkalis cause it to split up into hydrocyanic acid, ammonia, and salicylic aldehyde. It melts at 168°, and at a higher temperature is decomposed into hydrocyanic acid and a resinous substance.

A somewhat similar substance is formed when an alcoholic solution of salicylic aldehyde is heated with ammonium cyanate. It separates from the above solution in bright yellow needles, which are insoluble in water, but easily soluble in alcohol and ether. It melts at 143°, and is decomposed at a higher temperature. Analysis led to the formula $C_{22}H_{18}N_{2}O_{4}$. This substance is perhaps identical with the hydrosalicylamide of Reinecke and Beilstein. The author is continuing his investigations.

T. B.

Mutual Convertibility of Aromatic Mustard Oils (Sulphocarbimides) and Cyanides. By W. Weith (Deut. Chem. Ges. Ber., vi, 210—214).

Transformation of Phenyl Cyanide into Phenyl-sulphocarbimide.—It being considered probable that the addition of sulphur to an aromatic cyanide would convert it into the corresponding sulphocarbimide, a mixture of aniline, chloroform, and alcoholic potash was heated with excess of sulphur, in order that the phenyl cyanide formed might act on the potassium polysulphides simultaneously produced so as to form phenyl sulphocarbimide, which in reacting on a new portion of aniline would produce diphenyl-sulphocarbamide. The result was as expected, diphenyl-sulphocarbamide being produced, and on treating this with hydrochloric acid the phenylic-sulphocarbimide was obtained in the free state. Diphenyl-sulphocarbamide was also obtained by digesting a mixture of aniline and phenyl cyanide with alcoholic potash and sulphur, treating the product with dilute hydrochloric acid, and crystallising the residue. The hydrochloric acid used for its purification contained a base which in some of its properties agreed with triphenyl-guanidine. The mixture of aniline and phenyl cyanide when heated with sulphur alone also yielded diphenyl-sulphocarbamide, and during its formation by this process an odour resembling that of bitter almond oil (benzonitrile?) was observed. An attempt to prepare phenyl-sulphocarbimide by the direct action of sulphur on pure phenyl cyanide did not give very satisfactory results, but some oily drops were obtained which appeared to consist of phenylic sulphocarbimide.

Transformation of Tolyl Cyanide into Ditolyl-sulphocarbamide.—When a mixture of toluidine, chloroform, and alcoholic potash is treated with sulphur, a reaction similar to that already described takes

place, and almost the theoretical amount of ditolyl-sulphocarbamide is produced.

Benzonitrile and Sulphur.—No reaction was observed when these substances were heated together.

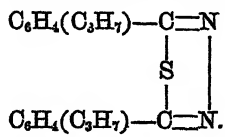
Desulphurisation of Phenyl-sulphocarbimide.—When this compound is digested with finely divided copper, it loses its sulphur, phenyl isocyanide being apparently formed, but this is afterwards changed by the action of the heat into its isomeride, benzonitrile. Phenyl isocyanide is converted into benzonitrile when it is heated in a sealed tube to 200°—220° for three or four hours.

Other sulphcarbimides when heated with copper lose sulphur. These reactions are still under investigation.

T. B.

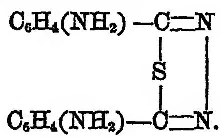
Thiamides. By R. WANSTRAT (Deut. Chem. Ges. Ber., vi, 332).

Action of Iodine on Thiocuminamide.—When a solution of iodine in alcohol is added to an alcoholic solution of thiocuminamide, until the former is no longer decolorised, and the alcohol is removed by distillation, an oil remains behind, which, after washing with water containing ammonia, solidifies to a white, amorphous mass. After several crystallisations this substance was obtained in transparent, colourless prisms, melting at 45°. Analysis led to the formula—



This substance is not acted on by dilute alkalis, dilute acids, or lead oxide; it is insoluble in water, but dissolves readily in ether, alcohol, chloroform, carbon sulphide, or sulphuric acid, and it is precipitated from the last-named solvent by the addition of water. Long boiling with aqueous potash or soda causes it to split up into sulphur and cumonitrile, and the latter substance is afterwards decomposed into ammonia and cuminic acid.

Action of Iodine on Amido-thiobenzamide.—These substances were made to react on one another, as in the previous instance, and the alcoholic solution, when evaporated, yielded a brown mass, from which boiling water extracted a substance which was deposited in white needles. Analysis led to the formula—



This substance melts at 128°—129°, and is soluble in alcohol, ether, carbon sulphide, chloroform, and benzene. It yields crystalline salts with hydrochloric acid and sulphuric acid, and the analysis of a double

platinum salt showed that the hydrochloride contains two molecules of HCl.

The action of iodine on thiocinnamide is now being studied by the author.

Action of Nascent Hydrogen on the Product of the Action of Iodine on Thiocuminamide.—An alcoholic solution of the above product was digested with zinc and hydrochloric acid, until no more hydrosulphuric acid was produced. The product was then treated with potash-solution, the alkaline liquor was agitated with ether, and the residue left when the ether was distilled off was extracted with boiling water; the aqueous solution deposited on cooling a small quantity of a substance crystallising in quadratic leaflets, which contained 89·64 per cent. of carbon and 9·21 per cent. of hydrogen. No platinum salt was obtained by treating this substance with platinum chloride.

A second experiment was made, in which alcohol, the product of the action of iodine on thiocuminamide, hydrochloric acid, and zinc were digested together for about ten days; the acid liquid was agitated with ether; and on fractionating the ethereal liquid, benzene and benzonitrile were found to be present.

The compound obtained by the action of iodine on amido-thiobenzamide was also subjected to the action of nascent hydrogen, but the product was not obtained in a state fit for analysis.

T. B.

Action of Hydrochloric Acid Gas on the Compound Ammonias.

By C. LAUTH (Compt. rend., lxxvi, 1209—1212).

THE colour known as *violet de Paris* is produced by the action of oxidising agents upon methyl- and dimethyl-aniline. These bases are prepared by heating aniline hydrochloride with wood-spirit. Hofmann has stated that the methylaniline obtained by this process contains toluidine, and that the colouring matter is produced by the simultaneous oxidation of methyl-aniline and methyl-toluidine, just as magenta is formed by the oxidation of aniline and toluidine. He has since discovered that methyl-aniline at a high temperature is converted into toluidine, and this fact seems to support his view.

Lauth, however, observes that it is in opposition to the fact that the purer the aniline employed the greater is the proportion of violet obtained; also that the colour is produced equally well with methyl-aniline, prepared by the action of methyl iodide upon aniline, at a temperature much below that indicated by Hofmann as necessary for the methylisation of the phenyl-group in aniline.

The author has also made some experiments, with the object of showing that the methyl-anilines employed in the manufacture of Paris violet contain neither toluidine nor methyl-toluidine. He finds that when dry hydrochloric acid gas is passed into boiling methyl-aniline, gaseous methyl-chloride is produced, and, on cooling, a crystalline mass remains, consisting of aniline hydrochloride, free from toluidine.

Methyl-toluidine treated in the same way, gives methyl-chloride and toluidine, without a trace of aniline.

These results prove that the methylaniline employed in the manu-

facture of the violet does not contain either toluidine or methyl-toluidine, and consequently that Hofmann's opinion cannot be maintained.

He suggests the general application of the reaction with hydrochloric acid for the recognition of alcoholic groups, and for distinguishing isomeric organic bases.

W. A. T.

Action of Chloracetyl Chloride on Aniline and Toluidine.

By D. TOMMASI (Compt. rend., lxxvi, 885).

ANILINE and toluidine, when acted on by chloracetyl chloride, exchange an atom of hydrogen for the group C_2H_2ClO, giving rise to two new bodies, phenylchloracetamide, $\left.\begin{matrix} C_6H_5 \\ H \\ C_2H_2Clo \end{matrix}\right\} N$, and benzylchloracetamide, $\left.\begin{matrix} C_7H_7 \\ H \\ C_2H_2Clo \end{matrix}\right\} N$. These bodies are obtained by adding aniline or toluidine in small quantities to chloracetyl chloride, kept cool.

Phenylchloracetamide crystallises from its aqueous solution in fine needles, and from alcohol in tables. It melts at 97°, and sublimes at a higher temperature. It dissolves freely in ether and acetic acid, and easily in hydrochloric and sulphuric acids on warming. Nitric acid converts it into a nitro-compound.

Benzylchloracetamide crystallises in prismatic needles, which sublime at 110°, and melt at 162°. It dissolves sparingly in boiling water, and more freely in hot sulphuric and acetic acids, but not in hydrochloric acid. With nitric acid it appears to yield a nitro-compound.

J. R.

Separation of Toluidine and Pseudotoluidine.

By R. BINDSCHEDLER (Deut. Chem. Ges. Ber., vi, 448).

THE firm of Dalsace frères, in Paris, prepare a "heavy aniline" boiling between 198° and 200°, consisting mainly of toluidine and pseudotoluidine; these may be approximately separated thus: 2500 grams of oxalic acid are dissolved in 25 litres of boiling water, 6 litres of strong hydrochloric acid are added, and 10 kilogs. of this heavy aniline; the whole being allowed to cool to 60°, a mass of crystals forms, from which crystalline toluidine of melting-point 45° can be obtained by distillation with soda. Two kilogs. more of oxalic acid are added to the filtrate, whereby a further precipitate of crystals is formed, consisting of a mixture of the oxalates of toluidine and pseudotoluidine; the bases regained from this are used over again. The filtrate is treated with more oxalic acid until no more crystalline salt is produced (usually this further treatment is unnecessary); it then furnishes commercially pure pseudotoluidine containing no more than traces of aniline and so little toluidine, that no acetotoluidine separates even when large quantities are operated on.

C. R. A. W.

Derivatives of Pseudotoluidine. By E. GIRARD (Deut. Chem. Ges. Ber., vi, 444).

Dipseudotolylcarbamide, $CO\left\{\begin{matrix}NH.C_7H_7\\NH.C_7H_7\end{matrix}\right.$, is obtained either by heating urea and pseudotoluidine together, or by the action of carbonyl chloride on pseudotoluidine; it crystallises in fine white needles, and forms *dipseudotolyl sulphurea* and carbon oxysulphide when heated to 200° with carbon disulphide.

Tripseudotolyl-guanidine, $C\left\{\begin{matrix}NH.C_7H_7\\N.C_7H_7\\NH.C_7H_7\end{matrix}\right.$, may be obtained from dipseudotolylurea by heating with phosphorus trichloride and pseudotoluidine; or from the corresponding sulphurea by heating with pseudotoluidine alone, or with pseudotoluidine and oxide of lead; it is insoluble in water, soluble in alcohol and ligroin, and melts a little above 100°. When heated to 180° with carbon disulphide, it forms *dipseudotolyl sulphurea* and *pseudotolyl-sulphocarbimide*.

$$C\left\{\begin{matrix}NH.C_7H_7\\N.C_7H_7\\NH.C_7H_7\end{matrix}\right. + CS_2 = C\left\{\begin{matrix}NH.C_7H_7\\S\\NH.C_7H_7\end{matrix}\right. + N\left\{\begin{matrix}CS\\C^7H^7.\end{matrix}\right.$$

The latter is best obtained, however, from the sulphurea by heating with strong hydrochloric acid, thus—

$$C\left\{\begin{matrix}NH.C_7H_7\\S\\NH.C_7H_7\end{matrix}\right. + HCl = N\left\{\begin{matrix}C_7H_7\\H\\H\end{matrix}\right..HCl + N\left\{\begin{matrix}CS\\C^7H^7.\end{matrix}\right.$$

It is a colourless strongly refractive liquid boiling constantly at 239°, and readily forms sulphureas with amines; thus with solid toluidine it forms a sulphurea crystallising in white silky needles, decomposed by strong hydrochloric acid into paratoluidine and pseudotolylsulphocarbimide. Phenyl-sulphocarbimide and pseudotoluidine give a sulphurea decomposed by hydrochloric acid into aniline and *pseudotolylsulphocarbimide*, which latter forms the normal dipseudotolyl-sulphurea when treated with pseudotoluidine.

Chlorocarbonic ether and pseudotoluidine form oily *pseudotolyl methane*; this, when heated with phosphoric anhydride, forms *pseudotolyl cyanate* boiling at 186°.

C. R. A. W.

Tetramethyl-aniline from Coal-tar. By S. SESEMANN (Deut. Chem. Ges. Ber., vi, 446).

IN a coal-tar colour factory a bye-product was obtained in the manufacture of methylaniline. After several crystallisations from ligroin, it formed white crystals melting at 87° and distilling unaltered: it had the properties of a nitrile base, and appeared to be $N\left\{\begin{matrix}C_6H_3(CH_3)_2\\CH_3\\CH_3\end{matrix}\right.$

C. R. A. W.

Violet Derivatives of Rosaniline. By A. W. HOFMANN (Deut. Chem. Ges. Ber., vi, 263—264).

HOBRECKER prepares a new aniline-violet by acting with benzyl chloride and methyl iodide on a solution of rosaniline in methyl alcohol. The compound thus obtained has the composition $C_{20}H_{16}(C_7H_7)_3N_3.CH_3I$, and forms beetle-green needles, which are almost insoluble in water, and dissolve sparingly in cold, more freely in boiling alcohol.

C. S.

Action of Ethyl Oxalate on Naphthylamine. By M. BALLO (Deut. Chem. Ges. Ber., vi, 247—251).

THE reaction between these bodies is different according as it takes place between the dry substances or in presence of alcohol.

When 1 mol. of ethyl oxalate is heated to 90° with 1 mol. (or better with 2 mol.) of naphthylamine and a little 90 p.c. alcohol in a sealed tube for two or three hours, the product is *naphthylammonium naphthyloxamate*, formed according to the equation—

$$C_2O_2{}^{OC_2H_5}_{OC_2H_5} + 2C_{10}H_7NH_2 + H_2O = 2C_2H_5OH + C_2O_2{}^{NHC_{10}H_7}_{OHC_{10}H_7NH_2}.$$

Naphthylammonium naphthyloxamate crystallises from alcohol, and better from hot water, in dry, fine, white needles, which melt at 154°, undergoing rapid decomposition. It is soluble in chloroform, carbon sulphide, and ether. Warm dilute hydrochloric acid dissolves and decomposes it, setting free naphthyloxamic acid. The aqueous solution gives with calcium chloride a precipitate of calcium naphthyloxamate.

When, on the other hand, naphthylamine is heated to boiling for some time with excess of dry ethyl oxalate, and the product, after cooling, is exhausted with boiling alcohol, the solution thus formed deposits crystals of *ethyl naphthyloxamate*, whilst the undissolved residue consists of a white pulverulent substance nearly insoluble in ordinary solvents, melting at 231°, and subliming at a somewhat higher temperature in delicate, white, often iridescent, crystals. The reaction in this case is represented by the equation:—

$$C_2O_2{}^{OC_2H_5}_{OC_2H_5} + C_{10}H_7NH_2 = C_2O_2{}^{NHC_{10}H_7}_{OC_2H_5} + C_2H_5OH.$$

Ethyl naphthyloxamate crystallises from alcohol in needles. It melts at 106°. It appears to be insoluble in water, but dissolves easily in chloroform and carbon sulphide, and sparingly in ether.

Free *naphthyloxamic acid*, $C_2O_2{}^{NHC_{10}H_7}_{OH}$, is obtained by dissolving the foregoing naphthylammonium-salt in hot weak hydrochloric acid, from which solution it crystallises in tufts of fine white needles. It dissolves easily in alcohol, less freely in ether, and with difficulty in water. It melts at 180°, undergoing decomposition. Its salts undergo decomposition when heated, evolving vapours which smell strongly of

naphthylamine, and leaving a residue of carbon. The *potassium-salt* is obtained by dissolving the acid in hot solution of potassium hydrate, not too strong. It is deposited on cooling in beautiful anhydrous crystals. The *barium-salt*, obtained by saponifying the ethyl-compound with baryta-water, is a white crystalline powder, insoluble in water. The *calcium-salt* is obtained by adding calcium chloride to a solution of the naphthylammonium-salt.

When alcoholic solutions of 1 mol. of methyl oxalate and 2 mols. of naphthylamine are mixed at ordinary temperatures, a mass of crystals is formed consisting, not of a derivative of oxamic acid, but of *neutral naphthylamine oxalate*. The crystals when heated give off carbon oxide and dioxide and naphthylamine, whilst Zinin's oxanaphthalide and formamide are produced. The reaction between methyl oxalate and naphthylamine is represented thus:—

$$C_2O_2{}^{OCH_3}_{OCH_3} + 2C_{10}H_9N + 2H_2O = (C_{10}H_9N)_2H_2C_2O_4 + 2CH_3OH.$$

J. R.

The Alkaloids of Cinchona Bark. By O. Hesse (Ann. Chem. Pharm., clxvi, 217—278).

The author reviews at considerable length his own researches and those of other chemists on the following alkaloids: quinine, conchinine, quinidine, cinchonidine, cinchonine, aricine, paricine, quinamine, paytine, and amorphous alkaloids.

Normal quinine sulphate crystallises from water with $7\frac{1}{2}H_2O$; the author believes that it really contains $8H_2O$, but is very efflorescent; from alcohol it crystallises with only $2H_2O$.

Mono-acid quinine sulphate contains $C_{20}H_{24}N_2O_2.H_2SO_4 + 7H_2O$ (Gerhardt); $+ 7\frac{1}{2}H_2O$ (Kraut); the author confirms Gerhardt's formula. Six-sevenths of the water of crystallisation is given off in the exsiccator; the last $\frac{1}{7}$ at 100°—115°; the salt is soluble in 11 parts of water at 13°, and is less soluble in alcohol.

The di-acid sulphate contains $C_{20}H_{24}N_2O_2.2H_2SO_4 + 7H_2O$. Pure quinine hydrochloride is soluble in dilute nitric acid without any marked change of colour, but if it is mixed with 5 per cent. of morphine hydrochloride, an orange-red tint is produced; 1 per cent. gives a dark yellow colour, whilst 0·2 per cent. produces a marked change in the tint produced. The acid should contain 20 per cent. HNO_3 by volume.

The author finds the mean specific rotatory power of pure quinine (prepared in a variety of ways) in alcoholic solution to be—

$$\alpha_j = -165{\cdot}79 \text{ at } 15°$$
$$= -162{\cdot}46 \text{ at } 25°$$

To obtain the pure alkaloid it is not necessary first to convert it into herapathite, crystallisation from hot water sufficing to remove the last traces of impurity. The specific rotatory power of quinine in the form of salts is higher than when free, the more so the greater the quantity of acid present, and the higher the temperature.

Thus the sulphate gives the values—

$\alpha_j = -\ 191{\cdot}47$ in alcoholic solution
$-\ 228{\cdot}78$ dissolved in 6 molecules of H_2SO_4 diluted till $SO_3 = 4$ per cent. of the volume.

Whence the rotatory powers for the contained quinine are found to be—

$\alpha_j = -\ 220{\cdot}43$ in alcoholic solution
$-\ 264{\cdot}66$ in excess of sulphuric acid.

The mono-acid sulphate gives the value for the contained quinine.—

$\alpha_j = -\ 264{\cdot}30$ in alcoholic solution,

or sensibly the same as the acid solution of the sulphate.

With excess of acid the mono-acid sulphate gives higher values—

With 1 molecule SO_3 α_j for contained quinine $= -\ 277{\cdot}23$
" 3 " " $= -\ 280{\cdot}77$

The diacid sulphate gives—

$$\alpha_j = -\ 287{\cdot}62,$$

the value being the same whether excess of acid is present or not.

Similarly, the addition of excess of hydrochloric acid raises the rotatory power of the hydrochloride.

Crystallised $C_{20}H_{24}N_2O_2 \,.\, HCl + 2H_2O$, dissolved in alcohol gave—

$$\alpha_j = -\ 166{\cdot}41,$$

in water with large excess of acid $\alpha_j = -\ 247{\cdot}39$

Conchinine has the rotatory power (mean, in alcoholic solution)—

$$\alpha_j = +\ 260{\cdot}65.$$

Pasteur found for the red ray, $\alpha_j = +\ 250{\cdot}75$ at 13°, which gives for the yellow ray $\alpha_j = +\ 327°$. The sulphate, $2C_{20}H_{24}N_2O_2,H_2SO_4 + 2H_2O$, gives for the alkaloid present nearly the same value, viz.:—

$$\alpha_j = +\ 261{\cdot}18$$

but in presence of 1 and 6 molecules of excess of acid, it gives the values—

$$\alpha_j = +\ 323{\cdot}06$$
$$\text{and } \alpha_j = +\ 324{\cdot}54$$

The hydrochloride gives the values respectively for the alkaloid present—

In alcoholic solution	$\alpha_j = +$	270·03
In aqueous solution with excess of dilute acid	$\alpha_j = +$	312·47
Dissolved in fuming acid	$\alpha_j = +$	257·52

Cinchonidine hydrochloride crystallises in monoclinic double pyramids, a form not exhibited by the hydrochloride of any other cinchona alkaloid. It is obtainable in asbestos-like prisms of composition $C_{20}H_{24}N_2O_2HCl + 2H_2O$. The sulphate crystallised from alcohol contains $2C_{20}H_{24}N_2O_2.H_2SO_4 + 2H_2O$.

The author finds—

$\alpha_j = -$ 112·49 for the base dissolved in alcohol,
$-$ 178·47 for that contained in the sulphate dissolved in alcohol.

Presence of excess of sulphuric acid does not increase the rotation but slightly diminishes it.

For the hydrochloride—

$$\alpha_j = -162 \quad \text{in alcoholic solutions}$$
$$= -169{\cdot}29 \ \text{with excess of acid}$$

The hydrocinchonine of Willm and Caventou, obtained by the action of permanganic acid on cinchonine, is not precontained, but is an alteration-product.

The specific rotatory power of cinchonine is—

In alcoholic solution....................	$\alpha_j = +$	226·48
Neutral sulphate in alcoholic solution......	+	244·12
" " with 1 molecule free acid	+	261·49
" " " 6 " "	+	255·86
Hydrochloride in alcoholic solution	+	203·58
" in strongly acid aqueous solution	+	233·52

The author considers the question of the existence of the alkaloïd *aricine* as open.

Some qualitative reactions and notes concerning *paricine* are given, but no numerical values, save that it begins to cohere at 100° and fuses at 116°.

Quinamine forms long white anhydrous prisms of composition $C_{20}H_{26}N_2O_2$; its hydriodide is $C_{20}H_{26}N_2O_2.HI$, and is anhydrous; the hydrochloride, sulphate, acetate, tartrate, acid tartrate, mercurochloride, and mercuro-iodide, platinochloride, and aurochloride have been obtained. Its rotatory power is—

$$\alpha_j = +106{\cdot}8$$

Paytine is $C_{21}H_{24}N_2O_2$; its rotatory power is—

$$\alpha_j = -49{\cdot}5$$

By the action of heat, the crystallisable alkaloïds are converted into amorphous isomerides.

C. R. A. W.

Action of Hydrochloric Acid on Codeine. By C. R. A. Wright (Chemical News, xxvii, 287).

This paper gives the results of a series of experiments made with a view to elucidate the changes which take place in codeine by the continued action of hydrochloric acid. In many respects these changes are, as might be expected, analogous to those which take place in morphine when submitted to the same treatment (Mayer and Wright, this Journal [2], xi, 211); but in some points the action is of a different character.

The first action of hydrochloric acid on morphine appears (*loc. cit.*) to give rise to an addition-product ($\overline{M}$ + HCl).2HCl (where $\overline{M}$ is

morphine, $C_{34}H_{38}N_2O_6$), from which the elements of water are subsequently removed, the final product being a body of composition $(\overline{M} + 2HCl - 2H_2O).2HCl$; homologous compounds $(\overline{C} + HCl).2HCl$ and $(\overline{C} + 2HCl - 2H_2O)2HCl$ (where $\overline{C}$ = codeine, $C_{36}H_{42}N_2O_6$) are similarly produced when codeine is treated for a short time with hydrochloric acid at 100°. A mixture of hydrochlorides is thus obtained from which sodium carbonate throws down a mixture of bases $(\overline{C} + HCl)$ and $(\overline{C} + 2HCl - 2H_2O)$; these are soluble in ether and form non-crystalline salts; the second is the "chlorocodide" of Matthiessen and the author (*Proc. Roy. Soc.*, xviii, 83).

In just the same way the first action of hydrobromic acid on codeine is found to give rise to the corresponding bases in the bromine series, viz. $(\overline{C} + HBr).2HBr$, and $(\overline{C} + 2HBr - 2H_2O).2HBr$, the latter being the "bromocodide" of the author (*Proc. Roy. Soc.*, xix, 371 and 504); in properties these bases exactly resemble the chlorinated bases of analogous composition.

By the long-continued action of hydrochloric acid on the mixture of bases thus resulting when codeine and hydrochloric acid are heated together, different results appear to be formed according to the circumstances of the experiment; it has been shown by Matthiessen and the author that by acting on codeine or the product of the action of HCl on that alkaloid in sealed tubes at 140°—150° with strong hydrochloric acid, methyl chloride is formed, and "apomorphine" results, *identical with that obtained from morphine* (*Proc. Roy. Soc.*, xvii, 460, and xviii, 83). When, however, the action is allowed to take place at 100°, different bodies result; methyl chloride is eliminated, but the elements of water are not removed to such an extent as to produce "apomorphine:" two isomeric bases are formed, intermediate in composition between morphine and "apomorphine;" one yields crystalline salts, and is readily soluble in ether, the other is insoluble in that menstruum, and gives amorphous salts, and evidently belongs to the "tetra" series. The two bodies are, therefore, considered to have respectively the formulæ—

$$C_{68}H_{72}N_4O_{10} \ldots = (\overline{M}_2 - 2H_2O).$$
$$C_{136}H_{144}N_8O_{20} \ldots = (\overline{M}_4 - 4H_2O).$$

and are respectively termed *diapo-dimorphine* and *tetrapo-tetramorphine*. In physiological effects, diapo-dimorphine does not resemble tetrapo-dimorphine ("apomorphine,") the experiments of Dr. J. G. Blackley indicating that doses of 0·1 gram given subcutaneously to cats do not produce vomiting but only profuse salivation. The removal of the elements of water from (hypothetical) dimorphine and from tetramorphine gives rise to a different kind of alteration in the physiological effect (on cats) of the resulting product, the emetic action being *less* in the first case the more of the elements of water are removed, and *more* so in the second case; thus—

Di-Series.

Name of base.	Relation to morphine.	Physiological action.	Observer.
Dimorphine	$\overline{M}_2$	?	—
Diapo-dimorphine ..	$\overline{M}_2-2H_2O$	Produces profuse salivation, but no vomiting (cats)	Dr. J. G. Blackley.
Tetrapo-dimorphine..	$\overline{M}_2-4H_2O$	Moderately powerful emetic (cats): very powerful emetic (man)	Drs. Gee and Stocker.

Tetra-Series.

Tetramorphine......	$\overline{M}_4$	Very powerful emetic (cats)	Dr. Stocker.
Diapotetramorphine .	$\overline{M}_4-2H_2O$	Powerful emetic (cats and dogs)	Ditto.
Tetrapotetramorphine	$\overline{M}_4-4H_2O$	Produces profuse salivation, but no vomiting (cats)	Dr. Blackley.
Octapotetramorphine	$\overline{M}_4-8H_2O$	Neither salivation nor vomiting (cats)	Ditto.

The concluding part of the paper is devoted to a series of tables giving the classification of the above derivatives and of the others obtained from codeine as starting-point in the author's previous researches (in some cases in conjunction with the late A. Matthiessen): these tables (a continuation of those given on page 228 of this volume for the derivatives previously obtained from morphine as starting-point), are too lengthy for reproduction here, wherefore the reader is referred to the original paper, or to the *Deut. Chem. Ges. Ber.*, vi, 268, where the tables are given *in extenso*.

C. R. A. W.

Solanine in Solanum Lycopersicum. By G. W. Kennedy (Pharm. J. Trans. [3], iii, 606).

The alkaloïd was separated in the following manner. A quantity of the living plant, leaves and stems, was bruised to a pulp in a mortar, and the pulpy mass then macerated for 48 hours in water strongly acidulated with sulphuric acid. The liquid was then expressed, and the maceration repeated. After being expressed as before, the two liquids were mixed, and after standing for some days filtered and treated with dilute solution of ammonia in excess. The precipitate which formed was separated by straining, dried in heated air at 120° F., and then boiled several times with alcohol. The alcoholic solution, filtered while hot, deposited on cooling small feathery crystals of solanine, which had a smell like potatoes, and a taste rather nauseous, bitter, and somewhat sweetish. With sulphuric acid, the alkaloïd gave a bright red colour,

passing into reddish-brown, and with iodine a characteristic yellowish-brown colour was produced.

J. B.

Hydrastis Canadensis or Golden Seal and its Alkaloïds.

(Pharm. J. Trans. [3], iii, 604).

THE rhizome of Hydrastis canadensis is used medicinally as a bitter tonic analogous to calumba. It contains two alkaloïds, viz., *berberine* (also found in the barberry calumba root and elsewhere), and *hydrastine*. The former is well known.

The latter crystallises in white shining four-sided prisms, which lose their transparence upon dessication. It is very bitter and pungent, and provokes in the mouth a feeling of numbness which causes it to be employed in America as a local anæsthetic. Nearly insoluble in water, it is freely soluble in alcohol, ether, chloroform, and benzene. As the last three do not dissolve berberine, the hydrastine may be easily extracted by treating the powdered root in a displacement apparatus with either of these solvents. The proportion so obtained is about one and a half per cent.

A substance prescribed in America under the name of *hydrastine*, is said to be a mixture of hydrochlorate of berberine and hydrastine.

J. B.

Starch and Albumin.

By S. ROTHER (Pharm. J. Trans. [3], iii, 644).

THE following experiment shows that in presence of starch, albumin is held perfectly in aqueous solution at a boiling temperature, and that only a strong acid can then separate it from such a solution.

Pure starch (fifty grains) was mixed with water (one fluid ounce), and the albumin of one egg was diluted with water to three fluid ounces, and strained through muslin. Then after uniting the clear albumin solution with the starch, the mixture was subjected to prolonged boiling; no precipitation, however, occurred, the liquid having only the opalescent appearance of starch-water. The solution filtered quite readily, yielding a clear and transparent filtrate. A drop of strong nitric acid added to this instantly produced a dense gelatinous white coagulum. The solution, when diluted and treated with nitric acid, immediately gave an abundant precipitate of white bulky flakes which rapidly settled down, leaving the supernatant liquid clear.

J. B.

Excretin.

By F. HINTERBERGER (Ann. Chem. Pharm., clxvi, 213—216).

THIS compound was discovered by Marcet, who gave to it the formula $C_{78}H_{156}SO_2$; but the body thus formulated is a mixture; pure excretin contains no sulphur and consists of $C_{20}H_{36}O$. It is obtained by exhausting fresh excrements with boiling alcohol and allowing the solution to stand for a week. A black precipitate then separates out

containing some excretin and the salt $C_{58}H_{113}MgNO_{11}$. The filtrate is precipitated with milk of lime and the dried precipitate treated with a hot mixture of ether and alcohol. On exposing the solution during a week to a temperature below 0°, crude excretin crystallises out in semi-globular masses consisting of yellow needles. It is purified by crystallising it repeatedly from alcohol, with addition of blood-charcoal, the temperature being kept below 0°. Bromine converts it into *dibromexcretin*, $C_{20}H_{34}Br_2O$, separating from a mixture of ether and alcohol in hard brittle crystals grouped in globular masses. A crystalline chlorine-compound could not be obtained. 100 pounds of fresh excrements yielded 8 grams of pure excretin.

C. S.

Composition of Wool-fat.

By ERNST SCHULZE (Deut. Chem. Ges. Ber., vi, 251—254).

THE author finds that the fat of wool contains, besides cholesterin, a second alcohol isomeric with it, for which he proposes the name *isocholesterin*. The most remarkable property of this body is that it crystallises from ether and acetone in fine transparent needles, but separates from its solution in alcohol in gelatinous masses or white flocks. It melts at 137°—138° to a colourless liquid which does not crystallise on cooling. Like cholesterin it dissolves easily in hot glacial acetic acid, and the solution deposits on cooling white flocks of an unstable compound of isocholesterin with the acid. Mixtures of cholesterin and isocholesterin melt at a temperature 10°—15° lower than either body alone, and do not crystallise on cooling.

Besides the above substances, wool-fat appears to contain another alcohol of lower melting point, which has not yet been isolated.

J. R.

Physiological Chemistry.

On the Properties and Composition of a Cellular Tissue Diffused throughout the Organism of the Vertebrata. By A. MÜNTZ (Compt. rend., lxxvi, 1024).

WHEN the skin of a mammal is exhausted with boiling water, a residue is left cors'sting mainly of connective tissue. This tissue, like cellulose, is soluble in ammoniacal cupric sulphate, but it also dissolves in an ammoniacal solution of zinc oxide which has no action on cellulose. It is insoluble in ammonia. Sulphuric acid converts it into glycocine. Potash appears to produce from it neither leucine nor tyrosine. Its composition is that of the albuminoids.

W. A. T.

On some Chemical Reactions of Active and Inactive Muscles.
By PAUL GRÜTZNER (Pflügers Archiv., vii, 254—263).

IN order to ascertain whether a muscle during or after a period of activity would abstract oxygen from other substances, as it does from blood, the author made several experiments with a solution of indigo. Sometimes he passed this through the vessels of a frog, one leg of which had been tetanized for some time while the other was at rest. At other times he rubbed up the muscles with the solution. Both methods gave somewhat irregular results. He therefore rubbed up the muscles with pyrogallic acid and filtered. The filtrate from the active muscle is invariably colourless or pale-yellow, but that of the inactive is brownish. Other experiments showed that the difference in the reaction of the muscle is not sufficient to explain this, and therefore that the inactive muscle oxidizes pyrogallic acid to a considerable extent quite independently of its reaction, while the active muscle hardly exerts any oxidizing power at all. The albuminates in muscle are the chief causes of this oxidation. A still better reagent than pyrogallic acid alone was found by the author to be a mixture of one volume of a 0·5 per cent. solution of pyrogallic acid and half a volume of a 0·1 per cent. solution of ferric chloride. Oxidizing substances render it brown in a similar manner to pyrogallic acid, while reducing substances, such as zinc, copper or iron turnings, ammonium sulphide, sulphites, glycerin, uric acid, &c., change it to a fine deep violet. When muscles are rubbed up with this liquid and filtered, the filtrate obtained from a muscle which has been contracting is of a clear violet colour, while that from an inactive muscle is reddish-brown. The former retains its colour for a considerable time while the latter becomes still browner after exposure to air, and the difference between the colour of the liquid thus increases after a few minutes. This would appear to show that muscles which have been contracting have a reducing action. This, however, is not the correct interpretation of the reaction, for the violet coloration occurs when a ferrous salt is used instead of a ferric salt in the preparation of the reagent. The author believes that the violet colour is due to the formation of ferrous pyrogallate. This is formed when finely-divided metallic iron is dissolved in pyrogallic acid. The reason why it is not formed when a ferrous salt is used, is that pyrogallic acid has extremely feeble acidulous properties and cannot separate the iron from the stronger acid with which it is already combined. But if a little alkali be added to the mixture, so as to liberate ferrous oxide and enable the pyrogallic acid to combine with it, a purple colour is at once developed. An additional quantity of alkali makes the mixture reddish-brown, as the free pyrogallic acid then becomes brown and this colour becomes mixed with the violet.

The reducing substances already mentioned act in a similar way, as they either have an alkaline reaction or transform the acid salt of iron into a basic salt with which the pyrogallic acid can combine. Thus the acid reaction of the ferric chloride solution is much diminished by agitation with zinc turnings, zinc chloride and free ferric oxide being formed. The latter is reduced by the pyrogallic acid which then combines with it. Uric acid has the power of driving out stronger acids

and forming compounds with basic salts of iron. It forms with the ferric oxide an insoluble basic compound which can be decomposed by pyrogallic acid. Glycerin also diminishes the acidity of acid solution of ferric chloride and promotes the formation of the violet compound.

As ferrous salts in solution tend to become basic, their solutions when mixed with pyrogallic acid become blue on exposure to air, though no coloration occurs at first. Ferrous pyrogallate is also formed when a salt with a strong base and a weak acid is added instead of an alkali to the mixture already mentioned. The author considers that the violet coloration which is produced in a mixture of pyrogallic acid with a ferrous or ferric salt by an active muscle, although it is also produced by many reducing substances, is no sign of reduction, but depends on the presence of lactates in the muscle.

When the quantity of iron in the mixture is increased four-fold or more, the reaction is different. In such a fluid the inactive muscle produces a violet coloration as well as the active one. This effect is due as before to lactates in the case of the active muscle, but in that of the inactive one to the alkali it contains. When little iron is present, the alkali gives rise to browning of the pyrogallic acid, but when there is a large quantity of a salt of iron, the whole of the alkali becomes combined and even set free. The violet ferrous pyrogallate is thus formed, and the browning of the acid prevented. The blue colour is less when the muscle is pounded with a solution of sodium chloride, filtered, and the reagents added to the filtrate, or when it is bruised in pyrogallic acid and the iron salt afterwards added. This is not the case when the reverse method is adopted. The author has also occasionally observed another reaction. When a muscle which has been in action is pounded in a 0·1—0·5 per cent. solution of ferric chloride to which a trace of alkali may be added, the faintly-brownish solution becomes yellow. This is also due to the lactates present. This reaction was observed in frogs caught in summer, but not in those caught in winter. This may be due to the different quantities of lactic acid present in the muscles under these conditions.

T. L. B.

Composition of the Grey and White Substances of the Brain.

By D. PETROWSKY.

THESE researches, which were undertaken in Professor Hoppe-Seyler's physiological laboratory, consisted of two analyses, for each of which four bullocks' brains, as fresh as possible, were used. The grey layer was separated from the white by means of water and a portion of the white matter was taken from the interior. Each substance was rubbed up rapidly in a mortar, and three extracts and a residue were obtained by digesting it respectively in cold alcohol, ether, and hot alcohol. Omitting numbers, the components of these extracts and residue, are seen from the following table:—

1. *Cold alcoholic extract* contains:—
   a. Substance insoluble in anhydrous ether.
   b. " soluble " "

2. *Ether extract* together with *a.* (*sic*) contains :—
   Lecithine,
   Cholesterin and fats.

3. *Warm alcoholic extract* contains :—
   Lecithine,
   Cerebrine.

4. *Residue* contains :—
   Albuminous substances,
   Salts.

The method employed in estimating the lecithine from the magnesium pyrophosphate was that recommended by Hoppe-Seyler.

No sugar could be detected in the portion of Extract 1, insoluble in anhydrous ether (a).

The author gives a table showing the average composition from the two analyses of the grey and white substances respectively, from which it appears that the dried *grey substance* consists about half of albumin, a quarter of cholesterin and fats, and very little cerebrine, its principal components, therefore, being albumin and water. In the *white matter*, on the contrary, cholesterin and fats form much more than half the dried mass, albumin a quarter of the whole substance, and cerebrine is present in considerable quantity.

E. C. B.

Metamorphosis of Bones. By C. Aeby (J. pr. Chem. [2], vii, 37—44).

The author appears to regard bone as made up in great part of a complex molecule, in which the lime and phosphoric acid bear a constant relation, but in which the excess of lime over orthophosphate is sometimes wholly combined with carbonic acid, and sometimes is partly carbonate and partly hydrate.* In fossil ivory half the excess of lime exists as hydrate. Fossil bones contain less carbonic acid and more fluorine than fresh bones, but the proportion of lime to phosphoric acid is unchanged. The enamel of teeth is mainly composed of orthophosphate, with only a little carbonate; the tooth-bone contains the usual excess of lime, of which the greater part exists as hydrate. The enamel of ancient teeth from the lake-dwellings of the stone age is found changed into vivianite; the tooth-bone and other bones are, under the same circumstances, merely penetrated with ferrous carbonate, and have taken up much fluorine. The gain in fluorine is always associated with the deposition of iron. Increase in fluorine is also connected with the presence of organic matter in the soil; bones found in gravel contain little fluorine, while those in peat-bogs are scarcely removed from apatite in composition. Bones long buried contain much less magnesia than fresh bone. From the great solubility of the magnesia in bone

* The author's idea is not expressed very distinctly; that fresh bone should contain calcium hydrate is quite contrary to the results of Wildt and others, who state that bone always contains more phosphoric and carbonic acids than are required to form ortho-salts.—R. W.

(compare *Jour. Chem. Soc.* [2], ix, 80) it appears probable that it occurs as carbonate.

R. W.

Brittleness of the Bones in Horned Cattle. By J. NESSLER (Annalen der Landwirthschaft, 1873, 126—127).

IN some places horned cattle, when fed on certain kinds of fodder, suffer from an unusual brittleness of the bones. Nessler finds:—

1. That in the hay which produces such brittleness the protein bodies are usually deficient. 2. All the suspected hay was poor in sodium. 3. In a peculiar sort of hay, very apt to produce the brittleness in question, the amounts of phosphoric acid and of calcium were very small. 4. The waters drunk by the affected cattle contained but a small quantity of mineral matter. 5. In the Black Forest the disease existed only upon granite soils, variegated sandstone, and the junction of the granite and gneiss.

T. S.

Chemical Constituents of the Eggs of Reptiles. By HILGER (Deut. Chem. Ges. Ber., vi, 165).

THE yolk of the egg of the common snake contains a proteïd resembling myosin, lecithin and its products of decomposition, cholesterin, alkali-albuminate. 8—9 per cent. of fat, phosphates, chlorides and sulphates of the alkali-metals. The shell contains carbonate and phosphates of calcium, traces of silica and iron, but no manganese; calcium sulphate is present, and indeed appears to be a general constituent of the body of lower animals as it exists in the outer integument of Holothuriæ, Tunicatæ (*Pyrosoma ind.*), Salpæ, Phallusiae, &c.

The shell and yolk also contain an organic substance consisting of C. 54·68, H. 7.24, N. 16·37, and O. 21·10. This body is free from sulphur and phosphorus, and forms in the dry state a yellowish, horny mass, insoluble in alcohol, ether, acetic acid, and dilute hydrochloric acid; with water it softens and swells up. The composition is similar to that of elastin, from which it differs, however, by not being acted upon by concentrated caustic potash.

C. S.

An Analysis of the Luminous Organs of the Mexican Cucŭyos. By CARL HEISSEMANN (Pflüger's Archiv. für Physiologie, vii, 365).

THE author, after suggesting that the scarcity of observations on the luminous organs of the Lampyridæ is due to the small size of the specimens obtainable by European observers, and that the larger size of the American Pyrophora admits of further investigations on the subject, details his own researches. These were made on the abdominal luminous organs of 186 large cucŭyos. The analysis of the ash was, however, only qualitative.

The organs, after being carbonised at a low heat were treated with boiling water. The water was found to contain phosphoric acid and

potash, also traces of chlorine, and on the addition of hydrochloric acid a gas was given off, whose nature could not be determined owing to the small quantity. The residue, insoluble in water, was almost entirely soluble in hydrochloric acid, and distinct evidence of carbonic acid and lime in it was obtained.

Uric acid occurs in these organs in two combinations, first as calcium urate, forming the granular masses; and secondly, as potassium urate, which is referred to the crystalline portion. The carbonic acid contained in the insoluble ash residue may be regarded as the product of combustion of the uric acid, and the phosphoric acid is, in the author's opinion, derived from the luminous cells; but the important question whether it occurs preformed and combined with potash, or is produced by the combustion of organic bodies containing phosphorus cannot be determined from his analysis.

Here, the author considers, is the starting point for future investigations.

E. C. B.

On the Presence of Dissolved Earths and Phosphoric Acid in Alkaline Blood. By A. P. FOKKER (Plüger's Archiv., vii, 274—284).

ALTHOUGH several authors have advanced the hypothesis that earthy phosphates are combined with albumin in blood, and by this means are kept in solution, no one has succeeded in producing earthy albuminates. The author has, however, obtained albuminate of lime and albuminate of magnesia. The former may be produced by filling a test-tube for one or two inches with filtered white of egg and strewing on the surface of this a thin layer of powdered lime. In a few hours a stiff jelly begins to form at the line of junction of the two surfaces, and gradually thickens. This is then removed by breaking the test-tube and freed from the excess of lime by washing. A still easier method of obtaining it pure is to place filtered white of egg in a flat basin, place a piece of filter-paper on the surface, and strew powdered lime upon it. In a few days a layer of translucent jelly forms on the under side of the paper. This lime-albuminate is quite free from excess of lime. Lime-albuminate is soluble in water, in a solution of sodium chloride, and in phosphoric acid. On dissolving in phosphoric acid, hydrogen sulphide is evolved. It is insoluble in calcium chloride and sodium carbonate. Its solutions in sodium chloride are precipitated by boiling or by acids. Its watery solutions are not coagulated by boiling, except after the addition of neutral salts. They are precipitated by acids, the precipitate being soluble in excess. They are precipitated by carbonic acid, the precipitate being soluble in alkalis and alkaline carbonates. The precipitate is due to albumin, which is separated by the combination of the acid with the earth. The salt formed by the acid and earth usually remains in solution. When carbonic acid is employed the calcium carbonate is dissolved by the excess of that acid, if the solution is sufficiently diluted; and the addition of an alkali or alkaline carbonate dissolves the free albumin and removes the turbidity which it occasions. The whole of the lime and and part of the albumin is pre-

cipitated from solutions of lime-albuminate in water, acetic, or phosphoric acid by ammonium oxalate.

Magnesia-albuminate is formed by allowing a mixture of white of egg and magnesia to stand for some hours. It is soft, slimy, and much more soluble in water than lime-albuminate. Concentrated aqueous solutions become turbid on boiling, but do not coagulate. Dilute solutions remain clear when boiled, and coagulate only after the addition of concentrated solutions of salts. They are precipitated by acids, including carbonic acid. The precipitate is dissolved by a little potash or ammonia. Potash or soda causes the precipitation of magnesia and the formation of alkali albuminate. Ammonia precipitates only part of the magnesia, and the addition of a phosphate afterwards causes a further precipitate. When an aqueous solution of lime-albuminate is precipitated by carbonic acid, the precipitate dissolved by sodium carbonate, and sodium phosphate added to it, a clear sometimes opalescent fluid is obtained, which will remain for many days unchanged and has a strongly alkaline reaction. It contains lime, which can be precipitated by ammonium oxalate. The alkaline reaction of the liquid shows that the lime is not present as phosphate, and the fact that the solution may be boiled or kept several days *in vacuo* without becoming turbid shows that the lime is not present as carbonate dissolved in excess of carbonic acid. It is present as lime-phosphate-albuminate. The alkaline reaction can be due only to alkaline carbonates (or phosphates). The addition of free alkali causes a precipitate of calcium phosphate. If a solution of lime-albuminate is mixed with sodinm phosphate the phosphoric acid combines with the lime, and soda, which again destroys the newly-formed compound, is set free; but if the lime-albuminate is first precipitated by an acid and sodium phosphate then added, the acid used in the precipitation neutralises the soda, which is set free, and the lime-phosphate-albuminate remains in solution.

It is possible to obtain acid solutions of albuminates, although these become gradually converted into syntonin. This is shown by the two following reactions. When a piece of lime-albuminate is dissolved in dilute phosphoric acid, the filtrate contains calcium phosphate and albumin; on the addition of sodium phosphate or carbonate, till the reaction becomes alkaline, a precipitate of calcium phosphate is thrown down, although no free alkali is present. This is due to the conversion of the lime-albuminate into syntonin by the prolonged action of the acid. When a solution of lime-albuminate is acidulated with phosphoric acid and sodium phosphate added, sodium carbonate produces no precipitate, and only free alkali is able to throw down the calcium phosphate.

That lime-albuminate is present in blood is shown by the fact that serum behaves exactly like solutions of lime-albuminate, *i.e.*, it can be preserved for some time *in vacuo* without depositing calcium phosphate; but this is gradually thrown down by caustic alkalis and precipitated by ammonium oxalate. The serum must be much diluted before the caustic alkali is added, as an albuminate is otherwise apt to form which interferes with the deposition of the precipitate.

The author believes that all the lime in the serum is present as lime-

albuminate, and that no other lime compounds exist in blood. For his criticisms of Pribram's research we must refer to the orignial. The author's experiments were verified by Professor Heynsius of Leyden.

T. L. B.

The Composition of Human Milk. By THEODORE BRUNNER (Pflüger's Archiv. f. Physiologie, vii, 440—458).

AFTER criticising several published analyses and methods of analysing milk, Brunner gives copious details of the methods employed by himself in his analyses. His mode of determining the amount of nitrogenous substances is somewhat new.

The milk is made just acid with dilute acetic acid, and the fluid, having been brought to the boiling point, is saturated with a neutral salt (magnesium sulphate, or if the sugar has to be determined, sodium sulphate). From time to time, as the milk again becomes alkaline, so much acetic acid is added as is requisite to keep the fluid acid. The mass is then cooled, thrown upon a filter, and is then easily washed with cold water. The dried coagulum gives the amount of nitrogenous substances *plus* the fat. The latter must be determined in a separate portion of the milk. Special precautions are given for the titration of sugar in the filtrate. The solids were determined after drying at 100° in a current of hydrogen.

The results do not appear to have been very accordant. They are here given in percentages:—

Albuminous bodies ..	0·18— 1·54;	mean	0·63
Fat	0·24— 4·41	„	1·73
Sugar	4·67— 6·93	„	6·23
Water	86·96—91·94	„	90·00
Soluble salts and extractives		„	1·41

Observations were also made on the differences between the secretions from the two breasts of the same person.

T. S.

On the Normal Microzymas of Milk, as the Cause of the Spontaneous Coagulation, and of the Alcoholic, Acetic, and Lactic Fermentation of that Liquid. By A. BÉCHAMP (Compt. rend., lxxvi, 654).

To observe the microzymas of milk, it should be diluted with five or six times its volume of creosoted water and filtered. The filter will retain a certain quantity of insoluble matter, which should first be treated with ether to dissolve out the butter, then with a dilute solution of sodium carbonate to take out a little casein, and lastly with distilled water. Under a power of 500 diameters, the microzymas may then be clearly distinguished.

Milk drawn direct from a cow into apparatus specially arranged to exclude the air, and kept at a temperature of 35°—40°, was found to be curded on the third day. At the time that the coagulation becomes clearly perceptible, no organism except microzymas can be detected

in the milk. Lactic acid, acetic acid and alcohol, are also found in milk curded under these circumstances, and the author therefore concludes, that the fermentation which is set up and produces these substances, is due to the microzymas normally present in the milk.

J. B.

The Presence of Bile-acids in Normal Urine.

By VOGEL and DRAGENDORFF (Zeitschr. Anal. Chem., xi, 467—469).

BY an extended series of experiments Vogel and Dragendorff demonstrate the presence of bile-acids as constituents, not only of pathological, but also of normal urine. Dragendorff extracted ·7—·8 gram of the acids from 100 litres of healthy urine.

T. S.

Production of Ozone in the Animal Organism. By Dr. BINZ (Chem. centr., 1873, 73—75).

SINCE ozone is destroyed by contact with organic substances, its formation in the living body would at first seem to be impossible; but yet there are many reasons for supposing that ozone is present in the tissues and possibly in the blood.

Ozone (represented by O_3, or rather an active atom O_1, joined to an indifferent molecule O_2 or H_2O) may be prepared in three ways, viz., by electricity, by means of certain peroxides by slow combustion.

In the animal body we have at least one of these means present for ozone-formation, *i.e.*, slow combustion; though possibly also oxyhæmoglobin may act after the manner of peroxides.

Vegetable protoplasm, nearly allied to animal protoplasm, has been shown to have the power of producing the ozone-reaction with tincture of guaiacum; so have certain animal tissues. The fact that ozone has never been detected in the living tissues is accounted for by the presence of albumin and other organic matters which have a greater affinity for ozone than is shown by guaiacum. A simple experiment proves this:—

Take two test-glasses, and in one place a few c.c. of white of egg. (neutralised with phosphoric acid or not), and in the other some water. Add ozonized water to each, and keep them for a few minutes at blood-heat; then add tincture of guaiacum, and the blue colour will appear at once in the glass containing no albumin, but no colour, or at the outside only the slightest possible trace appears in the other glass.

It is probable then that ozone is continually produced and used up again immediately in the animal tissues.

Other known facts of oxidation in the body point to the same conclusion. Sulphurous acid appears in the urine as sulphuric acid, $SO_2 + O_1 = SO_3$.

Uric acid takes up water and oxygen (ozone) and forms urea and carbonic acid—

$$C_5H_4N_4O_3 + 2H_2O + O_3 = 2CH_4N_2O + 3CO_2.$$

Also, according to Kerner, quinine becomes in the urine dihydroxylquinine (Qu + H_2O + O_1, or quinine + peroxide of hydrogen).

G. T. A.

Continuation of Researches on Respiration in the Lungs.

By MORITZ NUSSBAUM (Pflügers Archiv., vii, p. 296).

THE present research is a continuation of that of Wolffberg (see this Journal, 1872, p. 311), and has been undertaken for the purpose of confirming his conclusions, as the number of experiments on which he based them was rather small. The experiments were made in the same manner as those of Wolffberg and Strassburg. Wolffberg found the mean tension of the carbonic acid in the pulmonary vesicles to be 3·56 per cent., and in the venous blood of the right heart 3·43 per cent. The author found it to be 3·84 per cent. in the pulmonary vesicles, and 3·81 per cent. in the right heart. It is therefore certain that the tension of the carbonic acid in air confined within the lung and that of the venous blood in the right heart are identical. By filling the lungs with hydrogen, it was shown that no interchange took place between the air confined in that part of the lung experimented upon, and the remainder of the lung, and therefore the experiments were free from any fallacy that might arise from this source.

T. L. B.

The Respiration of Fishes.

By QUINQUAND (Compt. rend., lxxvi, 1141—1143).

A PURELY physiological paper on the relative amounts of oxygen absorbed by different species of fish under varying conditions. The author confirms the observations of Alex. Humboldt and Provençal that there is a cutaneous respiration in fishes; but it is feeble.

T. S.

Consumption of Water by Animals.

By M. HENNEBERG (Dingl. polyt. J., ccvii, 431).

THE author has observed that with an increased consumption of water by animals, a larger quantity is given off by the skin and lungs, and at the same time less of the carbohydrates of the food is assimilated, and more nitrogenous matter voided in the urine. It is, therefore, uneconomical to administer much water to fatting animals, or to keep them in hot stalls.

E. K.

Chemistry of Vegetable Physiology and Agriculture.

Distribution of Potash and Soda in Plants.

By E. PELIGOT (Compt. rend., lxxvi, 1113—1121).

THE author, continuing his researches on this subject, has endeavoured to ascertain whether plants, watered during the whole period of their

growth with solutions of sodium chloride or sodium nitrate, absorb any soda, and whether the ash of such plants differs in composition from that of those grown under the same conditions, but watered either with ordinary water or with solutions of potassium or magnesium salts. Haricots were grown in large pots in an ordinary garden soil, and each series received when necessary 10 litres of water or of the saline solutions indicated in the annexed table. During the first part of their growth the plants received 5 litres of solution containing 1 part of salt per 1000, and later, 5 litres containing 2 parts per 1000; in all 15 grammes of salt, equal to a dressing of about 3000 kilogs. per hectare. Duplicate experiments were made in each case. When the seeds were ripe, the entire plants were collected and dried, and the ash, which varied from 10 to 14 per cent. of the dried plant, analysed with the following results:—

Watered with.	Seine water.	Sodium chloride.	Potassium chloride.	Sodium nitrate.	Potassium nitrate.	Ammonio-magnesium sulphate.
Insoluble—						
SiO_2..........	7·2	15·2	13·6	10·4	12·1	13·0
CaO..........	29·6	26·5	22·7	21·8	18·5	24·9
$Mg_2P_2O_7$......	11·2	9·5	8·5	9·2	8·2	11·2
MgO	2·0	2·4	1·6	1·5	·9	2·0
CO_2..........	9·0	6·1	11·8	17·1	17·8	6·9
	59·0	59·7	58·2	60·0	57·5	58·0
Soluble—						
K_2CO_3........	33·0	6·6	4·5	28·3	28·2	23·8
KCl..........	·6	26·5	27·2	3·4	4·7	4·7
K_2SO_4........	7·4	7·2	10·1	8·3	9 6	13·5
	41 0	41 8	41·8	40·0	42·5	42·0

None of the ashes contained soda. The magnesium salt did not increase the magnesia in the ash; the magnesia and phosphoric acid were present nearly in the proportion to form ammonio-magnesium phosphate, the excess of magnesia shown in the analysis being principally due to the method employed. The potassium salts did not sensibly increase the quantity of potash in the ash, but the proportion of chlorine in the form of potassium chloride was very largely increased both by the sodium and potassium chlorides; this would seem to indicate that whilst the soil contained sufficient of the other mineral ingredients of plants, its quantity of chlorine was not in proportion to the assimilative power of the plants for that element.

E. K.

On the Inorganic Constituents of Sound and Diseased Potatoes.

By J. B. Hannay (Chem. News, xxvii, 147).

Three samples of potatoes yielded the following results: No. 1 consisted of good potatoes grown on well-drained, dark-coloured, mossy soil; No. 2, of potatoes from the same field, but much diseased and

quite unfit for human consumption, or even as food for cattle; No. 3, of potatoes from a field badly drained, and of a heavy clayey nature; all the tubers of this sample were more or less diseased, but they could mostly be used for human food:—

	No. 1.	No. 2.	No. 3.
Per cent. of ash	3·8	3·9	5·1
Soluble portion—			
Potassium	36·77	37·86	43·11
Sodium	3·24	3·12	0·68
Magnesium..............	1·87	—	0·04
Carbon dioxide	15 83	15·57	15·45
Phosphoric oxide	8·37	6·90	5·55
Sulphuric oxide..........	4·95	5·44	6·28
Chlorine	4·61	6·96	7·37
Insoluble portion—			
Silica	1·74	6·12	1·02
Ferric oxide and alumina..	0·62	0·89	1·17
Calcium	3·70	2·80	2·92
Magnesium..............	0 88	0·60	0·02
Carbon dioxide	2·90	1·45	1·34
Phosphoric oxide	3·70	3·06	6·20
Unburnt carbon..........	1·98	—	—
Oxygen, equivalent to metals *minus* equivalent proportion of chlorine	9·64	9·03	9·23
	100·80	99·80	100·38

It will be seen that the amount of potassium, chlorine, and sulphuric acid increase in the diseased root, whereas the soluble phosphoric acid decreases. On the appearance of disease, the starch-granules gradually diminish in size and number till, in the very badly diseased parts, only a confused mass of fibre remains. From his analyses and observations, the author concludes that the potatoe disease is a problem for the naturalist or the physiologist rather than the chemist.

J. B.

The Distribution of Alkaloïds in Cinchona Barks.

By P. Carles (Pharm. J. Trans. [3], iii, 643).

Various opinions having been expressed as to the seat of the alkaloïds in Cinchona barks, the author experimented upon barks of several species to afford additional information on the subject. The different layers were separated by means of a knife or a rasp, according to their texture and the thickness of the bark, and each layer was divided into two or three lots. The quinine was estimated as crystallised sulphate after heating to 100°; and the cinchonine and other alkaloïds, precipitated from the mother-liquor by ammonia, were weighed after desiccation at the same temperature. In the following tables, showing the results, the designation of the layers is not quite anatomically correct.

in consequence of the difficulty of separating them; but by cortical parenchyma is meant all the more external layers of the entire bark, and by liber the more internal.

C. calisuya (fine bark). In 1000 parts—

	Entire bark.	Cortical parenchyma.	Liber layers.
Quinine..........	20·40	23·40	13·20
Cinchonine	6·40	5·20	4·80

C. calisaya (thin barks)—

	Entire bark.	Cortical parenchyma.	Liber layers.
Quinine..........	17·70	20·70	14·40
Cinchonine	4·80	4·40	3·60

C. lancifolia (cortical parenchyma, thick and parenchymatous)—

	Entire bark.	Cortical parenchyma.	Intermediate layers.	Liber layers.
Quinine	8·10	24·60	11·10	6·60
Cinchonine..	3·60	5·50	4·80	3·20

New Granada bark (very fibrous, liber abundant)—

	Entire bark.	Cortical parenchyma.	Intermediate layers.	Liber layers.
Quinine	2·01	3·90	traces	none
Cinchonine..	11·20	7·60	8·40	8·00

Bright red bark—

	Entire bark.	Cortical parenchyma.	Intermediate layers.	Liber layers.
Quinine .. } Cinchonine } Quinidine }	20·25	21·60	11·20	14·80

C. succirubra—

	Entire bark.	Cortical parenchyma.	Intermediate layers.	Liber layers.
Total alkaloïds ..	45·40	36·60	23·20	16·40
Quinine	10·60	19·60	12·00	6·40
Cinchonine	34·76	17·00	11·10	10·00

From the large proportion of cinchonine present in this bark, the quinine is difficult to separate in the state of sulphate.

Huanuco bark—

	Entire bark.	Cortical parenchyma.	Liber layers.
Quinine..........	traces	traces	none
Cinchonine and Cinchonidine ..	51·40	47·00	45·7

Some authors have spoken of this bark as containing 5 to 6 parts of quinine per 1000.

Loxa bark—

	Entire bark.	Cortical parenchyma.	Liber layers.
Quinine..........	traces	traces	none
Cinchonine	2·20	1·40	traces

These results show that quinine exists in all parts of the bark, but in a much larger proportion in the external than in the liber layers; and analysis of the intermediate layers indicates that the proportion diminishes pretty regularly from the exterior to the interior. The seat of the cinchonine, however, does not appear to be so well established.

J. B.

Contributions to the Qualitative Analysis of Vine Leaves. By C. NEUBAUER (Zeitschr. anal. Chem., xii, 39—48).

THE leaves and young shoots of *Vitis vinifera* collected in June contained tartaric acid, acid potassium tartrate (about 1·1 per cent.), calcium tartrate, quercetin, quercitrin, tannin, starch, malic acid, gum, inosite, a fermentable and non-crystallisable sugar (about ·7 to 1·2 per cent.), calcium oxalate, ammonia, calcium phosphate and gypsum, besides several bodies not recognised. The above substances were in all cases identified by qualitative reactions only.

The aqueous extract of the leaves yielded by fermentation and repeated distillation a very fine wine bouquet.

Leaves collected in the autumn contained very much more quercetin, but only traces of quercitrin. Inosite and malic acid appeared also to be absent.

Using 50 kilos. of leaves, the author did not succeed in detecting pyrocatechin or glycollic acid, both of which were found by Gorup-Besanez in the leaves of the wild vine.

He is proceeding with his investigation.

M. J. S.

Preliminary Notice on the Isolation of the Bitter Substance of the Nut of the Karaka Tree (Corynocarpus lævigata). By W. SKEY (Chem. News, xxvii, 190).

THE nut of the Karaka tree is poisonous in its natural state, but yet it is one of the staple vegetable articles of food of the natives of New Zealand. After being gathered, the nuts are partially baked in earth-ovens, and then washed for some time in a stream of water. The poisonous matter is thus removed, and the nuts are then dried and stored for use.

The author has isolated the bitter substance thus removed by the natives, in the form of beautifully radiating acicular crystals. It possesses more the character and properties of a glucoside than of an alkaloïd, and it is proposed to call it *karakin*.

J. B.

Influence of Manures on Weeds. By R. Heinrich (Dingl. polyt. J., ccvii, 431).

The author in some manuring experiments on red clover, found the following percentages of weeds in the crops. Without manure, 57 per cent.; with ammonium sulphate, 30; sodium nitrate, 26; sulphuric acid, 18; magnesium sulphate, 10; sodium chloride, 7; potassium sulphate, 5·5; calcium carbonate, 4·9; quick-lime, 4·5; superphosphate, 4·4; and with gypsum 1·9 per cent

It would thus seem that lime manures, and especially gysum, exert a special action in helping the clover in its struggle for existence with other plants, besides increasing the yield; whilst nitrogenous manures are not so specifically favourable to clover but almost equally so to the other plants. Observations on the effect of different manures on the weeds in connection with other crops would be of great practical interest.

E. K.

Analytical Chemistry.

On Spectral Analysis and the Spectro-sodiometer. By Champion, Pellet, and Grenier (Compt. rend., lxxvi, 707—711).

The concentration of a sodium sulphate solution can be estimated by illuminating one-half of the field of vision of a spectroscope with a flame coloured by it, and the other half with a flame coloured by a solution of known strength, and then weakening the light of the first flame by means of a blue prism—the compensator—until the intensity of the light in both halves of the field of vision appears to be equal.

In order to graduate the instrument, solutions of sodium sulphate of known strength are taken, and the compensator, which is of varying thickness, is moved along a graduated scale until the same intensity of coloration is obtained as that produced by a sodium flame of constant intensity. The division of the scale which then coincides with the zero of the compensator, is marked with the number expressing the percentage strength of the solution used.

For details of the construction of the instrument, the figure and its description in the original paper must be consulted.

As the influence of varying quantities of potassium salts which may be present must be eliminated, all the solutions used for graduation are to be saturated with potassium sulphate, and the same must be done with the solutions in which the sodium is to be estimated; the whole of the sodium salt present must of course be converted into sulphate

Ashes of plants are first treated with sulphuric acid to remove carbonic and hydrochloric acids. By adding a slight excess of barium hydrate, all metals except sodium and potassium are removed as well as the sulphuric acid and phosphoric acid; the liquid is then exactly neutralised with sulphuric acid and finally saturated with pure potassium sulphate.

The exactness of the method can be seen from the following results :—

The mean of three determinations with 0·3 per cent. aqueous solution of soda gave 0·297 per cent. of Na_2O, and with a 0·6 per cent. aqueous solution of soda gave 0·63 per cent. of Na_2O.

R. S.

Use of the Sodium Monochromatic Light to appreciate the Changes of Colour of Litmus in Alkalimetry. By S. Henry (Compt. rend., lxxvi, 222—224).

Every chemist knows that it is almost impossible to observe accurately the change of colour in litmus by the light of a lamp or gas, and as alkalimetric determinations have frequently to be made in beet-root sugar manufactories during the night, the author imagined that it might be advantageous to employ a monochromatic soda flame for that purpose. On making the trial, it was found that the red solution of litmus appeared as colourless as water by this light, whilst the blue was as black and opaque as ink.

The author makes some remarks on its use for alkalimetric determinations with highly-coloured beet syrups, and recommends the employment of the monochromatic light in ascertaining the point of neutralization of coloured liquids generally.

C. E. G.

On the Determination of Oxygen in the Gases from the Lead Chambers, and on some new Apparatus used in Gas Analysis. By Max Liebig (Dingl. polyt. J., ccvii, 37—46).

Impressed with the importance of a ready method for ascertaining the amount of oxygen which escapes from the sulphuric acid chambers, and of the light which such determinations are capable of throwing upon the whole process of manufacture of oil of vitriol, the author subjected the different methods to comparative tests and found that the method proposed by Hart (*Zeitschr. f. anal. Chem.*, 1869, p. 482) of determining oxygen by means of freshly precipitated ferrous hydrate, likewise that by means of phosphorus, are both tedious and inaccurate. Scheurer-Kestner's method of employing nitric oxide, based upon the theory that the oxygen, by combining with the nitric oxide, forms only nitric peroxide, which is decomposed by the water present into N_2O_5 and N_2O_3, and that the latter becomes dissolved without decomposition, assumes that the amount of oxygen is found by dividing the number of the absorbed gas by 3, since one volume of oxygen unites with two volumes of N_2O_2 to form N_2O_4. Assuming, however, that one volume of oxygen by combining with four volumes of N_2O_2 forms only N_2O_3, and that the nitrous anhydride thus formed is soluble in water without decomposition, the number of cubic centimeters of absorbed gas would have to be divided by 5 instead of 3, in order to find the amount of oxygen present in the gaseous mixture. Numerous experiments made by the author with approximately equal mixtures of atmospheric air and nitric

oxide gave, however, the figure 4, instead of 3 or 5—the figures implied on the supposition that either N_2O_4 or N_2O_3 is exclusively formed in the reaction. On employing more N_2O_2 than air, he obtained a larger contraction, and by reversing the proportions a smaller contraction of the gaseous volume, a proof that the formation of N_2O_3 increases with the decrease of the proportion of oxygen in the gaseous mixture to that of the nitric oxide present. Hence varying quantities of oxygen must form varying volumes of N_2O_4 or N_2O_3, and no reliance can be placed upon this method. No such objections could be raised to the employment of an alkaline solution of pyrogallic acid. The formation of CO observed by Boussingault in gaseous mixtures very rich in oxygen (40 per cent.) is avoidable, however, according to Poleck (*Fres. Zeitsch. f. anal. Chem.*, 1869, p. 451), in mixtures containing only about 20 per cent. of oxygen, and could not possibly form a source of error in mixtures which like the gases from the acid chambers, rarely contain more than 6 per cent. of oxygen. The author constructed an apparatus which enabled him, by means of the same pyrogallate absorbent, to make an analysis every three minutes, and he found that, after having determined for five hours at intervals of five minutes, the oxygen which issued from a Gay-Lussac tower, the absorbent—pyrogallic acid—still indicated 20·6 per cent. of oxygen when the apparatus was charged with air instead of with the tower gases.

For a description of the complicated apparatus which the author devised, we must refer to the original, as it cannot be explained without diagrams. W. V.

Volumetric Estimation of Free Oxygen.

By P. Schützenberger and Ch. Risler (Bull. Soc. Chim. [2], xix, 152—156).

This paper gives fuller details of the method of estimating oxygen by means of hyposulphite (hydrosulphite) of sodium previously published by Schützenberger and Girardin (abstr. *J. Chem. Soc.* [2], xi, 88).

Preparation of the Reagent.—Hyposulphite (hydrosulphite) of sodium is formed by the action of zinc on acid sulphite of sodium, thus:—

$$3NaHSO_3 + Zn = NaHSO_2 + Na_2SO_3 + ZnSO_3 + H_2O.$$

After the reaction most of the sulphite of zinc crystallises out, the other products remaining in solution. The liquid, which absorbs oxygen with a rapidity comparable with that of pyrogallate of sodium, may be employed directly; or it may be converted into neutral hyposulphite by adding to it an excess of milk of lime, whereby the remainder of the zinc is thrown down as oxide, together with sulphite of calcium, whilst neutral hyposulphite of sodium (Na_2SO_2) remains in solution. The neutral salt absorbs oxygen much less rapidly than the acid salt. The following mode of operating is adopted by the authors:—A quantity of zinc in strips, twisted so as to occupy a large bulk, is placed in a wide-necked flask of 200 c.c. capacity, which is then filled with a solution of acid sulphite of sodium of 10° Baumé fully saturated with sulphurous acid; the flask is closed with a caoutchouc stopper perforated to allow the escape of air, and finally closed with a piece of glass rod. In about half an hour the reaction is complete, and the

solution may be at once diluted to about 2 litres for use if acid hyposulphite is desired. To obtain neutral hyposulphite, when necessary, the contents of the flask are poured into a 1-litre flask containing 30 grams of previously-slaked quick-lime and 600 c.c. of water; the flask is filled up with water and allowed to stand. When clear, the supernatant liquid, which should be feebly alkaline, is siphoned into a 2-litre flask half full of water.

Titration of the Hyposulphite.—The strength of the hyposulphite solution, whether acid or neutral, is determined by means of an ammoniacal solution of cupric oxide, which substance is reduced first to cuprous oxide and then to the metallic state by excess of the hyposulphite. Neutral or acid hyposulphite of sodium is converted by absorption of free oxygen into neutral or acid sulphite; but the authors have found that, in reducing cupric to cuprous oxide, the hyposulphite takes up only half as much oxygen as it would take up if the oxygen were free, and that consequently the product of the oxidation cannot be the same. They dissolve 2·23 grams of crystallised sulphate of copper in water, and add an excess of ammonia and enough water to make up the bulk to 1 litre. 100 c.c. of this solution represent 1 c c. of oxygen.

The titration of the hyposulphite may be made in an open vessel, 20 c.c. of the copper solution being employed. The point of the Mohr's burette containing the hyposulphite should be very long, so as to dip below the surface of the copper solution, and the reagent should be ran in rapidly, with constant stirring, till the blue colour changes to very pale yellow. The error due to atmospheric oxidation may be avoided by making the titration in a close vessel in a current of hydrogen or coal-gas deprived of oxygen. Comparison of the two methods has shown that this error amounts to about 0·5 c.c. in 20 c.c. of hyposulphite. The solution of hyposulphite is of a convenient strength when 20 to 30 c.c. of it are required to decolorise 20 c.c. of the copper solution.

The hyposulphite solution, the strength of which has been thus found, is employed at once to determine the amount of dissolved oxygen in water by plunging the point of the burette to the bottom of a vessel containing a litre of the water slightly coloured with Coupier's blue, and running in hyposulphite till the colour disappears, the two liquids being mixed with an agitator in such a way as not to disturb the surface. The free oxygen in water cannot be thus determined in an atmosphere free from oxygen, on account of the rapid loss of oxygen by diffusion; but this difficulty may be surmounted by introducing into a vessel filled with hydrogen, first an excess of the hyposulphite and then the water, and estimating the excess of hyposulphite by means of a solution of indigo of known strength, that substance being bleached by hyposulphite.

Solution of sodium hyposulphite, the strength of which is determined by means of oxide of copper, may obviously be employed for the volumetric estimation of copper. To avoid errors from dissolved oxygen, the authors boil the solution of copper to be estimated and allow it to cool in a current of gas free from oxygen, having first added enough carbonate of ammonia to re-dissolve the copper. A determination by this method gave 100·8 per cent. of copper.

J. R.

Volumetric Determination of Oxygen in Hydrogen Peroxide and other Liquids. By F. HAMEL (Compt. rend., lxxvi, 1023).

SOLUTION of permanganate of potassium is employed. The process is obvious.

W. A. T.

Detection of Ozone. By D. J. BOEHE (Deut. Chem. Ges. Ber., vi, 439).

PURE ozone can be obtained only by electrising dry mixtures of gases containing free oxygen. The oxidation of phosphorus in the air and the action of sulphuric acid on barium peroxide gives nitrous vapours and hydrogen peroxide.

Potassium-iodide-starch paper, brucine paper, and thallious oxide paper are convenient reagents.

Oxygen polarized by rapid combustion gives a vaporous body which is not absorbed by water, and rapidly blues starch-iodide paper, but has no action on thallious oxide paper; this the author considers may possibly be *antozone*. Nitrous acid, trioxide of hydrogen, ozone, or antozone may thus be produced by rapid combustion. By slower combustion (*e.g.*, when a hot glass rod is plunged into a vessel containing air and ether vapour.—Odling), "active oxygen" is formed, but whether ozone, hydrogen dioxide, or nitrous acid is produced has not been decided.

C. R. A. W.

Value of Tincture of Guaiacum as a Test for Ozone. By Dr. BENZ (Chem. Central., 1873, 75).

WE do not know the elementary composition of the blue colour produced in this reaction, and therefore it might as easily be a chlorine as an oxygen compound, though it is in all probability the latter.

The reaction may be produced by the addition of carbonic-acid water and bleaching powder to the tincture of guaiacum, but this is a case of oxidation: $CaCl_2O_2 + CO_2 = CaCO_3 + 2Cl + O$. With regard to the production of the blue colour by means of calcium chloride and sugar of lead, the author's experiments led him to conclude that this is not the case if the salts are perfectly pure. The reaction may be caused by impurities or by the presence of mould on the damp surface of the crystals from which the solution has been prepared, since Schönbein has shown the latter to be capable of producing the reaction.

G. T. A.

Proposed New Method of Estimating Carbon Dioxide. By A. HOUZEAU (Compt. rend., lxxvi, 773).

IF the gas be conducted into caustic soda-solution and the latter be then treated with neutral barium chloride and filtered, the loss of alkalinity, as determined by a standard acid solution, will represent the amount of carbon dioxide absorbed. If zinc oxide be dissolved in

the soda, the formation of bicarbonate, which may sometimes take place, will be indicated by the precipitation of zinc carbonate, in which case more caustic alkali must be added. No experiments or results are given, and it is not stated in what way the soda is protected from the atmosphere during filtration, &c.

B. J. G.

Estimation of Iodine in Presence of Chlorine or of Bromine.

By H. Hübner (Zeitschr. anal. Chem., xi, 397—402).

1. *In presence of Chlorine.*—Thallium iodide (TlI) is perfectly insoluble in cold water; thallium chloride is, however, soluble in this liquid. On these facts the author's method is based. To a cold dilute neutral solution of an alkaline iodide and chloride thallious nitrate solution ($TlNO_3$) is added drop by drop from a burette, with constant agitation of the liquid, until the precipitate changes in colour from yellow to white. The precipitate is collected, after 8—12 hours, in a weighed filter thoroughly washed with water, dried at 100°, and weighed as thallium iodide (TlI). To the filtrate silver nitrate is added, and the ensuing precipitate of silver chloride is collected and weighed as usual.

The author gives estimations which show that his method is possessed of a fair degree of accuracy.

2. *In presence of Bromine.*—The separation of iodine from bromine may also be effected by means of thallious nitrate, the process being conducted as in the preceding case. In a well-conducted experiment the error in the quantity of iodine found does not exceed 0·01 p. c.

The separation may also be effected by adding to the solution of alkaline iodide and bromide first a saturated, then gradually a dilute solution of lead nitrate until the precipitate just begins to change colour from yellow to white. After standing for 12—18 hours the precipitate, which is almost pure lead iodide, is collected in a weighed filter, washed thoroughly, dried at 110°, and weighed. The bromine is in the filtrate chiefly as alkaline bromide.

Especial care must be taken not to add more lead nitrate than is sufficient to precipitate all the iodide, since if lead bromide is also thrown down it will be necessary to add a considerable quantity of water to dissolve this bromide, and then the lead iodide will also be partly dissolved. Altogether this process is not so exact as the preceding.

Iodine and chlorine cannot be separated by the use of lead nitrate.

M. M. P. M.

A Generally Applicable Method of Determining Sulphur.

By A. Sauer (Zeitschr. anal. Chem., xii, 32—36).

The substance is burnt in oxygen, the products of combustion are collected in hydrochloric acid containing bromine, and the sulphuric acid is determined by barium chloride.

For fixed bodies (coke, &c.) a plain combustion tube is used, for volatile ones the tube is narrowed near the middle, the substance

placed in the longer end, and a carbonic acid apparatus attached. The cork at the other end carries two tubes, one reaching to the middle conveys oxygen, the other carries off the products of combustion to the absorption apparatus. The tube is first filled with carbonic acid and the narrow part heated; oxygen is then passed in, and the substance being now distilled burns at the narrow part of the tube. Finally the tube is swept out with carbonic acid or, if necessary, with oxygen. Any ash may be examined for sulphates. Caoutchouc is apt to leave zinc sulphide.

The author considers his arrangment more simple than that of Mixter (*Sill. Jour.* [3], 4, 90).

M. J. S.

Testing Phosphoric Acid for Phosphorous Acid, Nitric Acid, and Arsenic. By H. Hager (Zeitschr. anal. Chem., xi, 461—463).

Five c.c. of the Pharmaceutical acid are placed in a short test-tube with 4 c.c. of water and a piece of pure zinc; the test-tube is closed with a cork, having a slit, in which is fixed a slip of parchment-paper moistened with silver nitrate. If the paper is not darkened after two hours, both phosphorous acid and arsenic are absent. Hydrogen phosphide turns the paper brown; hydrogen arsenide, when in quantity, produces a black metallic stain; the presence of nitric acid greatly hinders the former, but not the latter reaction. Nitric acid may be recognised by treating the liquid poured from the zinc with excess of potash, and adding an alkaline solution of cupric oxide; if, on gently warming, cuprous oxide is precipitated, nitric acid was originally present; this is a delicate test. In the presence of nitric acid, a ferrous salt should be added with the zinc before testing for phosphorous acid. Sulphuric acid may be tested by the same processes if diluted with six times its volume of water.

R. W.

Estimation of Phosphoric Acid. By Camillo Schumann (J. pr. Chem. [2], vi, 416).

The author concludes from his experiments that it is not necessary to make any correction for the solubility of magnesium-ammonium orthophosphate in dilute ammonia liquor, provided that the liquor contain 2·5 grams of free ammonia (NH_3) per 100 c.c.

Fresenius considered that 0·001 gram should be added to the weight of magnesium pyrophosphate obtained for every 54 c.c. of ammoniacal filtrate; the author, on the other hand, finds the following numbers as means on estimating the phosphoric acid in equal bulks of a sodium phosphate solution diluted to different degrees with ammonia solution, so that in each case 2·5 grams of free ammonia were present per 100 c.c.

(1)	Diluted to	100 c.c.	Mean $Mg_2P_2O_7$	= 0·2297 gram.
(2)	„	500 „	„ „	= 0·2300 „
(3)	„	1000 „	„ „	= 0·2308 „

Were Fresenius' correction required, the result of (2) should be 0·0074, and that of (3) 0·0165 *less* than that obtained in experiment (1).

In other experiments solution of pure dibasic sodium phosphate was evaporated to dryness and weighed in sodium pyrophosphate; equal quantities of this solution were precipitated by magnesia liquor and weighed as magnesium pyrophosphate.

Found as sodium pyrophosphate (mean)	0·1171 gram	P_2O_5
" magnesium " "	0·1167 "	"

The author equally considers it unnecessary to dissolve the precipitated magnesium-ammonium phosphate in acid, and re-precipitate it with ammonia, as recommended by Kubel and by Heintz; thus the last-mentioned results were obtained with a single precipitation only, also the weight of pure magnesium pyrophosphate obtained by dissolving pure magnesium sulphate in boiling nitric acid, supersaturating with ammonia until the excess of ammonia equalled 2·5 grams per 100 c.c., and ignition of the precipitate, was always less than that of magnesium pyrophosphate taken at first; thus—

Taken 0·2294	Found after treatment as above	0·2283
" 0·2500	" " "	0·2470

The chance of the precipitation of magnesium compounds other than ammoniaco-phosphate is easily avoided by not adding a great excess of magnesia solution (100 grams magnesium sulphate, 100 ammonium chloride, 800 water, and 400 ammonia solution of sp. gr. 0·96 form a convenient liquor, of which 1 c.c. contains 0·1 gram magnesium oxide, representing 0·15 gram phosphoric acid); also, if the solution is warm, too high results are obtained when the precipitate is not re-dissolved.*

The author finds that the same results are obtained after the magnesium precipitate has stood 14 hours as when it is allowed to stand 7 days.

Uranium phosphate readily penetrates even thick filter-papers, and is difficult to wash; otherwise the gravimetric estimation of phosphoric acid by means of uranium gives good results.

The volumetric estimation of phosphoric acid by uranium, also, is capable of giving good results, provided the somewhat lengthy instructions of the author are complied with. Thus he obtained the following numbers:—

Gravimetric: by molybdic acid.	Volumetric: by uramin.
26·21	26·10
27·33 }	27·26 }
27·04 }	26·95 }
11·15	11·10
15·91	15·85

* In the estimation of phosphoric acid in iron-containing liquids, when the iron is kept in solution by citric or tartaric acid, the abstractor has found it *absolutely essential* to re-dissolve the first precipitate; otherwise traces of iron compounds, &c., are contained in the substance weighed.—C. R. A. W.

The phosphoric acid contained in phosphorite can be estimated with considerable accuracy by treating the pulverised mineral with sulphuric acid, supersaturating with ammonia, adding nitric acid, and precipitating by molybdic acid, &c. (Silica is not taken up, as would be the case were hydrochloric acid used, and the absence of ammonium chloride enables sharper results to be obtained); whilst that in manures, &c., may be estimated with sufficient accuracy for technical purposes by adding acetic acid and ammonia to the solution, filtering from ferric phosphate, precipitating calcium as oxalate, and throwing down the phosphoric acid in the filtrate by molybdic acid; the results are slightly in excess of the truth.

C. R. A. W.

Estimation of Phosphoric Acid as Uranic Phosphate.
By A. Kitchin (Chemical News, xxvii, 199).

The author states that with certain precautions this method is quite as accurate as the magnesium process, and possesses certain advantages over the latter. The estimation can be conducted in the presence of lime, &c., and the precipitate of uranic phosphate is almost completely insoluble in water containing ammonium acetate and free acetic acid. The principal precautions to take are to have a sufficient amount of ammonium acetate, and not too much free acetic acid. The precipitate should be dried and ignited strongly, until the filter is consumed. A little nitric acid should then be added, and the ignition repeated gently. If the ignition be carried too far, the uranic phosphate is partially reduced, and a second evaporation with nitric acid is necessary.

J. B.

Determination of Phosphoric Acid in Manure and Fossil Phosphates.
By C. Mène (Compt. rend., lxxvi, 1419).

A criticism of Joulie's recommendation that agricultural phosphates should be analysed by a suggested modification of the ammonium citrate method. The author himself recommends Chancel's (bismuth) method.

Joulie (*ibid.* 1488) replies to the above criticism, plainly showing that it has no application to his proposal. Chancel's method is not accurate in the presence of iron or aluminium.

R. W.

On the Detection of Arsenic.
By J. W. Gatehouse (Chem. News, xxvii, 189).

The following modification of Fleitmann's test is given as more useful and delicate than the usual mode of working. Place the solution in a long test-tube, and drop in a small piece of caustic soda about the size of a pea, also a piece of aluminium about a quarter of an inch in length by one-eighth of an inch in breadth, and cover the tube with a piece of filtering-paper, which has been moistened with solution of silver

nitrate. If the soda does not at once act with energy on the aluminium, warm gently and set aside for a short time. If arsenic be present, the silver nitrate will be blackened, but this will not take place if antimony alone be present. Should there be some quantity of arsenic, the whole solution will become of a dark brown colour, leaving a stain on the tube, owing to the separation of arsenicum; but with antimony alone a few black flakes, settling into a heavy black precipitate, are observed, the solution remaining colourless.

This test is so delicate that 0·0075 of a grain of arsenious acid, dissolved in soda and diluted with water to 250 grains, produces a perfectly characteristic reaction on the paper, the solution, however, remaining colourless.

J. B.

Testing Hydrochloric Acid for Arsenic. By J. B. Oster (Zeitschr. anal. Chem., xi, 463).

Boil with strips of pure tin-foil, and leave the liquid to cool. A trace of arsenic colours the liquid and stains the tin. The presence of ferric chloride produces somewhat similar appearances.

R. W.

Detection of Traces of Arsenic and Phosphorus in Toxicological Researches. By C. Neubauer (Zeitschr. anal. Chem., xi, 477).

Arsenious chloride is separated by Marsh's process. For the extraction of phosphorus, carbon disulphide is preferred.

T. S.

Detection of Arsenical Pigments in Carpets and Paper. By H. Hager (Zeitschr. anal. Chem., xi, 478).

A ready but untrustworthy method.

T. S.

Arsenic in Green-tinted Envelopes. By A. Vogel (N. Repert. Pharm., xxii, 166).

The author has found arsenic in green-tinted envelopes bought in Munich. These were apparently coloured with Schweinfurth green. A most convenient way of detecting arsenic is to dissolve in nitric acid the flakes left in Marsh's apparatus, add silver nitrate, and neutralise with ammonia, when silver arsenate is precipitated. Copper is readily found by treating the pigment with hydrochloric acid and adding a drop of solution of ferrocyanide of potassium, when the characteristic red-brown precipitate appears.

C. R. A. W.

On the Precipitation of Magnesia. By Dr. MOHR (Zeitschr. anal. Chem., xii, 36—38).

MICROCOSMIC salt is found to be a much better precipitant for magnesia than simple sodium phosphate added to an ammoniacal solution. The precipitate comes down crystalline at once, and may be filtered off immediately.

The precipitate produced by sodium phosphate consists at first of magnesium phosphate, which only slowly becomes crystalline by absorbing ammonia and water. Heat accelerates this change.

The author believes that ammonia exists in solution as NH_3, and must be converted into NH_5O before combining with the precipitate. He refers to the parallel case of the non-precipitation of a calcium salt by ammonium carbamate, which he explains in the same way.

M. J. S.

On the Estimation of Manganese by Weight. By R. FRESENIUS (Zeitschr. anal. Chem., xi, 413—427).

IN this paper the author examines the various methods used and proposed for the precipitation of manganese from solution. Exactly known quantities of the metal were taken for each experiment, and the weight of the precipitate obtained was controlled by determining the quantity left in the mother-liquor and wash-waters.

Guyard's method of throwing down the manganese as dioxide by addition of an excess of potassium permanganate was first tried, and, as might be expected, gave results considerably too high. W. Gibbs's method of precipitating by oxalic acid in presence of an excess of strong alcohol, and washing with nearly absolute alcohol, gave about 99 per cent. of the manganese present, the rest remaining in solution.

W. Gibbs's other plan of converting the manganese into phosphate of manganese and ammonium by adding ammonia in excess to the boiling acid solution containing sodium phosphate, and then washing with boiling water, after maintaining the whole for about an hour at the boiling-point, gave very constant and correct results, especially when cold water was used for washing and the quantity of the wash-water diminished as much as possible by the use of the sucking filter. The phosphate of manganese and ammonia is soluble in 32092 parts of cold, and in 20122 parts of boiling water. (The precipitate is ignited, and weighed as pyrophosphate.)

Precipitation as Manganous Sulphide.—The circumstances affecting the accuracy of this method were examined, with the following results:—1. A great excess of ammonia causes the results to come out a little too low. 2. Even a great excess of ammonium sulphide does no harm. 3. Great excess of sal-ammoniac interferes *slightly* with the precipitation. 4. Yellow ammonium sulphide is at least as good as colourless. 5. The presence of tartaric acid is of no effect. 6. Citric acid almost entirely prevents the precipitation of manganous sulphide.

In estimating the small quantities of manganese left in solution, it is customary to drive off the excess of sal-ammoniac by heat, but the author found that the latter body carried with it a very considerable

quantity of manganese. Hugo Tamm's method of precipitating with carbonate of ammonia was the last plan examined, and was found to give most excellent results, very little affected by the presence of even large quantities of sal-ammoniac.

C. H. G.

Examination of the Methods of Water-Analysis.

By TIEMANN (Deut. Chem. Ges. Ber., vi, 278—285).

THIS is the first part of an account of experiments upon the comparative value of the methods in use for the determination of the hardness of water and of the amount of sulphates, nitrates, organic matter, etc., contained in it.

As regards hardness, the older method of Clark gives more accurate results with the soap-test than the modifications introduced by Boutron and Boudet, and by Wilson.

The quantity of magnesium salts can be approximately found from the difference between the total hardness and the results of a volumetric determination of the lime-salts; but if accurate results are wanted, recourse must be had to the ordinary methods of gravimetrical analysis.

G. T. A.

On the Properties of some of the most frequently occurring Fat Oils of the Vegetable Kingdom with the methods of testing and detecting them.

By G. GLASSNER (Chem. Centr., 1873, 57—62).

THE author describes the difference between the drying and non-drying oils, and gives a short account of the most characteristic properties of the commonest ones.

The following table gives at a glance the ordinary reactions, and will serve for the detection of any of the commoner fat oils.

Table for the Detection of the Fat Oils.

	At the ordinary temperature.				After boiling.		
5 vols. oil and 1 vol. caustic potash 1·34 are well shaken together. The mass is:—	Snow-white: Almond oil: good rape oil, bleached. Olive oil.	Yellowish: Poppy oil, olive oil, rape oil. Sesame oil.	Greenish: Linseed oil; hemp oil: oils containing copper, and artificially coloured oils.	Rose: Refined rape oil.	Brown and solid: Hemp oil.	Yellowish-brown fluid: Linseed oil.	Red: Train oil.
Equal volume of oil and fuming red nitric acid are carefully poured into a test-glass. At the point of contact a ring is formed, and this is:—	Small and bright green, the oil itself is flocky and non-transparent. Almond oil.	Dark green, rose-coloured above. Poppy oil.	Broad and beautifully bright bluish-green. Olive oil.	Boron-red. Cod-liver oil.	Green, red above. Linseed oil.	Brownish-red, greenish below. Rape oil.	The whole of the oil is after a time coloured red. Linseed oil.
	10 drops of oil and 2 drops of acid.			Equal volumes of oil and acid.			
				Without carbon sulphide.			With carbon sulphide.
The oil is mixed with pure concentrated sulphuric acid in a test-glass; the point of contact between the two is coloured:—	Fine green, with brown streaks. Rape oil.	Yellow, on shaking, brownish olive-green. Poppy oil.	Red, soon passing into black serpentine streaks. Train oil.	After shaking, fine full dark green. Rape oil.	Green. Linseed oil. Hemp oil.	Red. Train oil.	With twenty times its volume of carbon sulphide, beautiful violet, quickly turning brown. Train oil.
By the elaidine test the oil becomes:—	Solid, curdy, white. Olive oil: almond oil: bleached rape oil.	Solid, curdy, yellow. Rape oil.	Solid and red. Sesame oil.	Wax-like white. Castor oil.	Streaks and drops of oil show themselves in the elaidine: a mixture containing drying oils.	Unchanged. Linseed oil, Poppy oil, Nut oil.	Ethereal oils added to improve smell of olive oil float on top of the elaidine.
By boiling with lead oxide and water, a plaster is formed, the consistency of which is:—	Solid: Olive oil.	Greasy: rape oil: almond oil. Sesame oil.	Greasy, but drying after a time. Drying oils.	—	—	—	—
Solubility of one part of oil in alcohol:—	1 : 1. Castor oil.	1 : 25. Poppy oil.	1 : 30. Hemp oil.	1 : 40. Linseed oil.	1 : 60. Almond oil.	—	—
Specific gravity:—	·913. Poppy oil, and oil of *Brassica napus*.	·914. Almond oil, and oil of *Brass. camp.*	·918. Olive oil.	·923. Sesame oil.	·926. Sunflower oil.	·950 . ·970. Castor oil.	·930. Linseed oil.
Temperature of liquefaction Centigrade:—	− 27°. Hemp oil.	− 18°. Castor oil. + 2·5°. Olive oil.	− 16° to − 20°. Linseed oil. − 20° to − 25°. Almond oil.	− 16°. Sunflower oil.	− 6°. Oil of *Brassica napus*.	− 4°. Oil of *Brassica campestris*.	− 5°. Sesame oil.

G. T. A.

Technical Chemistry.

The Salts employed by Voisin and Dronier, for the Bichrome Battery. By Th. Du Moncel (Dingl. polyt. Jour., ccvii, 483—487).

The inconvenience of transporting the bichrome battery has long been felt. Chutaux was the first to prepare a solid which should yield a solution capable of exciting the battery. The mixture employed by him was composed of equal parts of water, sulphuric acid, and potassium bichromate, evaporated nearly to dryness. Voisin and Dronier employed chemical equivalents of sodium sulphate, sulphuric acid, and potassium bichromate, $Na_2SO_4 + 7H_2SO_4 + K_2Cr_2O_7$. The use of the sodium sulphate is to solidify the mixture, and it may be viewed as a conveyer of acid. The chromium is deoxidised during the action of the battery, the resulting salt being a potassio-sodio-chromous sulphate, to which Voisin and Dronier assign a very improbable formula.

The proportions by weight are 20 grams of this salt dissolved in 100 grams water. If the battery is intended for long use, the solution should not be too strong, for the mean electromotive power is not increased thereby; yet the stronger the solution is, the more active will be the battery. This apparent contradiction may be ascribed to the action of the chrome alum, which possesses considerable electromotive power, resulting from the deoxidation of the chromic oxide.

The author finds that Chutaux's sand-battery, with the above-mentioned mixture of salts, shows a greater electromotive power, after a month, than the ordinary bichrome and sulphuric acid.

The electromotive powers of this battery compared with a Daniel's, is as 1·97 to 1; its resistance is about 900 mètres of wire, 4 mm. in thickness.

The cost of an element of this battery is about 1*s*. a year, provided the solution be used four times in succession, and the battery be in use six hours a-day. The zinc costs about $3\frac{1}{2}d$. If greater intensity be required, and a circuit of less resistance, the cost may have a maximum of 3*s*. 4*d*. a-year, including $5\frac{1}{2}d$. for zinc, of which 200 grams are used.

Voisin and Dronier prepare their mixture by dissolving the sodium sulphate in the sulphuric acid, with the aid of heat, and gradually adding the potassium dichromate. The mass solidifies on cooling, and may be cast into moulds. The various reactions take place as follows:—1. The oxidation of the zinc. 2. The reduction of the potassium dichromate by the nascent hydrogen. 3. Chromous sulphate is formed from the chromic sulphate. 4. The partial liberation of the potassium sulphate. 5. The formation of a chrome alum.

W. R.

Testing of Yellow Glass for the Dark-room of Photographers. By Le Neve Foster (Dingl. polyt. Jour., ccvii, 427).

A small strip of white paper, or of silver wire, placed on a black ground, is viewed through a prism, the glass under investigation being interposed between the paper and the prism. When yellow glass is employed, all blue lines do not disappear; ruby-red glass, however, absorbs all the blue and green of the spectrum, showing that it is best fitted for the purpose of absorbing the actinic rays, and thereby preventing chemical action.

W. R.

Sensibility of Haloïd Silver Salts to Light under Alkaline Development. By H. Vogel (Deut. Chem. Ges. Ber., vi, 89—92).

Although of the chloride, bromide, and iodide of silver, the last is the most sensitive photographic salt, a mixture of it with the bromide has been in use for years, in consequence of the greater sensitiveness of the bromide to faint lights, and to blue and green lights. Lea, however, some years ago, published a "dry" process, in which he employed the bromide alone, having found it to be the most sensitive to all lights. The observed greater sensitiveness of the bromide in this process has been attributed by Schultz-Sellack to a lesser degree of sensitiveness in the iodide in the "dry" process, as compared with the "wet" process, and an unchanged sensitiveness in the bromide.

The author has investigated the matter, and finds that both in the wet and dry processes the bromide is the most, and the iodide the least sensitive, when the developer, as in Lea's process, is an alkaline solution (pyrogallol and potash), the chloride being intermediate; and that the iodide is the most sensitive in white light, and the chloride the least, when an acid developer is employed (acidified silver nitrate, and either pyrogallol or ferrous sulphate). For shadows and coloured lights, the iodobromide is, with an acid developer, the most sensitive, but not with an alkaline one; for the wet process the author finds the proportion $5AgI + AgBr$ answer best, but for the dry process, $AgI + AgBr$.

E. D.

Improvements in Photolithography. (Dingl. polyt. J., ccvii, 429.)

Paul uses, in place of the ordinary mixture of gelatin and potassium bichromate, a mixture of equal parts of albumin and saturated solution of bichromate, with which he prepares the paper of the Autotype Company, which is admirably suited to the purpose. After exposure the unaltered albumin is dissolved out by means of cold water. By this method a much clearer and sharper image is transferred to the stone than by the usual methods.

E. K.

Phosphorescent Substances. By G. Seelhorst (Dingl. polyt. J., ccvii, 220—223).

The author has prepared a number of substances which exhibit phosphorescence.

1. *Green-phosphorescent.*—Strontium thiosulphate is heated for fifteen minutes over the bunsen lamp, and for five minutes over the blow-pipe.

2. *Blue-phosphorescent*—Strontium sulphate was mixed with a sulphate of unknown composition (prepared by decomposing strontium chloride), and the mixture reduced with hydrogen, and heated.

A number of other substances are enumerated. The author states that if these substances are mixed with melted paraffin and the mixture painted on to glass plates, imitations of flowers, &c., may be produced, which when placed against a black background and illuminated with magnesium light, appear very beautiful.

M. M. P. M.

Treatment of Dilute Chlorine. By W. Weldon (Dingl. polyt. J., ccvii, 512).

The dilute gas is passed over milk of lime in a state of agitation, so that equal parts of calcium chloride and free hypochlorous acid are formed. These products are treated with hydrochloric acid, evolving all their chlorine in the free state. Instead of lime, certain other oxides, and instead of hydrochloric acid certain metallic chlorides may be used, and are further claimed in the patent.

W. S.

On the Separation of Caustic Soda into portions of different strengths on passing from the Fused to the Solid State. By N. Glendinning and A. Edger (Chemical News, xxvii, 199).

When caustic soda containing water in excess of the quantity corresponding with that of its hydration passes from the fused to the solid state, it separates into portions of different strengths. A drum of caustic soda, containing 66·8 per cent. of soda (Na_2O) and about 6 per cent. water in excess of the water of hydration—as shown by the sample taken during packing—was cut through its centre transversely to its longitudinal axis, and samples taken as follows:—A, from the outside, not extending more than 1 inch towards the centre; B, from a part about 5 inches nearer the centre; and C, from the centre. The radius of the drum was 11 inches. The following are the results in percentages of soda (Na_2O):—

A.	B.	C.
66·9	69·7	61·6

The outside, or A sample, invariably agrees closely with the packing sample.

Analysis showed that the differences in strength are mainly attribut-

able to water, but also in some measure to chlorides and sulphates, these bodies occurring in largest quantities in the C or centre sample.

The differences in strength, due to separation, will be greatly influenced by circumstances, *e.g.*, the quantity of water present, the temperature at the time of packing, and the size of the drum.

The separation is deemed to be due to the superior affinity for water possessed by the partially fluid caustic soda over that on the point of solidification.

Ignorance of the preceding facts has frequently caused disputes between manufacturers and buyers as to the strength of the article.

J. B.

Process for precipitating Potash in the form of Alum from Colours intended for Roller-printing. By ERNST SCHLUMBERGER (Dingl. polyt. J., ccvii, 63—66).

IT continually happens that crystals of certain potassium salts, such as the chlorate, separate from the colours used for printing, and cause damage both to the rolls and to the goods. It is therefore useful to precipitate as much of the potassium as possible before preparing the colour. In many cases this can be done by addition of sufficient aluminium sulphate to form alum, which separates in crystals, leaving but a very small quantity of potash in solution, *e.g.*:—

$$6(KO.ClO_5) + 4(Al_2O_3.SO_3 + 18aq) = 3(Al_2O_3.SO_3) + (KO.SO_3 + 24aq) + Al_2O_3.ClO_5).*$$

To carry this out practically, dissolve 100 grams of potassium chlorate in 250 grams of hot water, and 362 grams of aluminium sulphate in 181 grams of water; leave both solutions to cool till they begin to crystallise; then mix, stir till cold, and strain off the crystals of alum, which amount to about 72 per cent. of the theoretical quantity. The aluminium chlorate so obtained has a density of 1.18° (22° Beaumé); it is strongly acid, and dissolves large quantities of gelatinous alumina, losing at the same time a great part of its acidity, and its tendency to decompose by heat. Red prussiate of potash treated in the same way gives a solution of aluminium ferricyanide, which is also strongly acid, and capable of dissolving much alumina.

C. H. G.

The Preparation of various Chlorates by help of Aluminium Chlorate. By BRANDT (Dingl. polyt. J., ccvii, 67—69).

SCHLUMBERGER having shown how to prepare aluminium chlorate, it becomes easy to prepare the chlorates of all bases which will precipitate alumina, *e.g.*, those of ammonia, lime, baryta, soda, or aniline, in a state of sufficient purity for the printer. The aniline chlorate so prepared is eminently adapted for the preparation of aniline black.

C. H. G.

* *Sic*; read $6KClO_3 + 4Al_2(SO_4)_3 = Al_2(ClO_3)_6 + 3Al_2K_2(SO_4)_3$.

Colours of Bricks.
By H. SEGER (Dingl. polyt. J., ccvii, 378—387).

THE author considers: (1) the colour of the mass of the brick, as seen by the fracture. The chief colouring ingredients are iron and manganese oxides. The former produces in the brick colours varying from light red to red-black, depending upon the amount of the iron oxide present, and also on the temperature to which the bricks are heated. If calcium carbonate be also present, silicates of iron, aluminium, and calcium are produced on heating, the colour of which changes as the temperature increases, from light red to yellow, then to flesh colour, and eventually to yellow or yellowish green. Manganese oxide is generally present in quantities so small as not materially to influence the colour of the bricks.

(2.) The colour of the brick near the exterior, in as far as this differs from the colour of the mass of the brick.

The colours here are much more uncertain than those of the mass of the brick. They are easily affected by the temperature, the gases from the fuel, &c. The surface of the brick often shows stripes or blotches of a red colour, while the inner part is yellow. These marks are caused by there being an insufficiency of lime to combine with the silicic acid, and so to form a silicate which can take up the greater part of the ferric oxide. The gases from the fuel, especially if coal is used, contain more or less sulphuric acid, which combines with the lime, thus fixing it as gypsum.

(3.) Substances derived from foreign sources sometimes cause the outer part of the bricks to be marked or coloured. These substances are either soluble salts formed by the action of the wash-water upon the clay (especially when this contains sulphates or chlorides), which remain on the bricks when these are dried, or they are part of the ashes from the furnace which are caught up by the wet surfaces of the bricks and are there fixed on drying.

(4.) After the bricks have been employed for building purposes, marks sometimes appear on their exteriors. These are caused either by the action of atmospheric moisture on soluble salts in the bricks, especially sodium bicarbonate, sodium and magnesium sulphates and chlorides (the presence of these salts being due to insufficiency of burning), or by the growth of small vegetable organisms on the bricks. These vegetable growths seem to confine themselves to light-coloured bricks; no sufficient means for their removal is yet known.

M. M. P. M.

Fire-resisting Power of various Clays. By CARL BISCHOF (Dingl. polyt. J., ccviii, 51—57).

THE author shows by a number of experiments, that when fireclays are ground to fine powder, mixed, when slightly moist, with varying amounts of powdered glass, made up into small cylinders, dried, and exposed to the action of heat, certain clays become fusible at much lower temperatures than others.

That clay which may be mixed with the largest per cent. of glass, and

yet remain infusible at a high temperature, is found to be, in practice, the best fire-resisting clay. Even small differences in the fire-resisting powers of various clays may thus be readily detected.

M. M. P. M.

Fireclays from Carniola. By A. Patera (Dingl. polyt. J., ccvii, 219).

Two clays were examined by the author, and both were proved to possess good fire-resisting properties. The analyses are as follows:—

	No. 1.	No. 2.
Insoluble in hydrochloric acid ..	94·00	91·50
Hydrated ferric oxide	1·50	2·91
„ aluminic oxide........	2·75	5·25
Lime, &c......................	traces	traces
Water.........................	1·75	0·34
	100·00	100·00

M. M. P. M.

The so-called Volcanic Building Stone. (Dingl. polyt. J., ccviii, 77.)

100 cwt. of coal ashes or slags, 16 cwt. of hydraulic lime, and 1 cwt. of Portland cement are worked together in a mill, and then pressed into moulds. The stone thus obtained withstands the action of the weather very well. The cost of preparation is low, and the stone possesses great strength. Stone prepared by this method has been used successfully in building houses, and the vaults and arches of certain churches; also in the erection of various other buildings.

W. S.

Porous Filters. By J. A. Wanklyn (Dingl. polyt. J., ccvii, 255—6).

A number of waters were filtered through silicated carbon filters, the amount of ammonia being determined before and after filtration. It is seen that the "free ammonia" increases, while the "albuminoid ammonia" decreases after each filtration.

These results seem to show that an accumulation of animal matter does *not* take place in the filter.

M. M. P. M.

The Copper Process of Hunt and Douglas. By Fr. Wimmer (Chem. Centr., 1873, 104).

This process for obtaining copper from its ores is now used in Chili and North Carolina. It depends upon the fact that cupric oxide in contact with ferrous chloride and common salt, is converted into cuprous chloride and ferric oxide, the former being soluble in the brine-solution. From this solution the copper is precipitated by scrap-iron, the

ferrous chloride solution remaining being used for treatment of a fresh portion of oxidised copper ore. The ore is stirred up in the vats to the consistence of mud; if it is very lumpy and granular, large vats should be used. The hot cupric chloride solution is allowed to flow through covered channels which contain scrap-iron, and through which sulphurous acid from the furnaces is passed by means of a jet of steam, to prevent formation of basic ferric chloride. If silver be present in the ores, it passes into silver chloride, and is dissolved by the brine, and may be precipitated by means of copper or potassium iodide.

The raw pyrites is first broken small, so as to pass through a sieve of 20 to 25 meshes to the inch, and then roasted in a reverberatory furnace with three beds. The treatment of the roasted ore in the agitating vats lasts about five hours, and the residue then contains from $\frac{1}{3}$ to $\frac{1}{2}$ per cent. of copper, the original ore containing on the average 5 per cent. W. S.

Preparation of Iron directly from its Ores. By P. TUNNER (Dingl. polyt. J., ccvii, 387—394).

THIS paper contains nothing new; it is merely an historical summary of the various methods of iron smelting, with especial reference to the processes of Siemens and Danks.

M. M. P. M.

Distribution of Carbon in Bessemer-Steel. By E. BELANI (Dingl. polyt. J., ccvii, 130—136).

IF the clean face of a section of rolled Bessemer-steel be treated with a dilute mineral acid, it is observed that the acid acts with a greater intensity upon some parts of the metallic face than it does upon others, the central portions being more strongly attacked than the outer ones. By the stronger action of the acid upon the centre of the sectional face, the latter becomes covered with a black dust, easily removed by washing. By this irregular action of acids, figures are delineated, which, with similar sections, are of surprising regularity. A number of samples of steel were treated with acid, as above, and borings were taken from the most distinctly marked sections of those parts most strongly and most faintly attacked. During the action of the acid, hydrogen and carburetted hydrogen are liberated, and separation of carbon takes place. This carbon arises mainly from that which is chemically combined in the steel, actual graphite being distinguishable in very small quantity only.

There is a striking difference in the mode of action of acids upon rolled and forged iron; by this action the former exhibits a large, strongly corroded centre or kernel, with a narrow and much less affected exterior, whilst with the latter the parts more or less strongly corroded are mingled together quite irregularly.

Estimations were now made of the amounts of carbon contained in the samples taken from those parts of a sectional face most strongly and also most faintly corroded by acid. The results obtained may be illustrated by the two following selected examples:—

	Mean of two analyses. Carbon per cent. faintly corroded portion.	Carbon per cent. strongly corroded.
Government railway iron, heavy section	0·2863	0·1432
Government railway iron, light section	0·3102	0·2147

According to the examples it is evident that those parts of the metal poorest in carbon are most rapidly acted upon by acids, whilst those richest therein are more slowly acted upon.

The specific gravity was observed to be greater in those portions where the action of the acid was weakest, and *vice versâ*.

Karsten gives the following facts:—If hardened steel be treated with dilute hydrochloric or sulphuric acids, it becomes covered after a long time with a black dust, unattracted by the magnet, and leaving no residue on ignition. It is therefore pure carbon, formerly chemically combined with the iron. In soft steel, the carbon is also chemically combined, but its relation to the iron is a different one. This steel treated with dilute acids leaves upon its surface a black residue of graphitic appearance, readily attracted by the magnet, and furnishing on ignition in the air 80 to 95 per cent. of ferric oxide. Treated for a longer time with acid, the iron is dissolved, and carbon alone remains. This is, therefore, a compound of carbon and iron, which Karsten names a polycarburet.

Percy states that the polycarburet existing in the solid iron can be decomposed by a red heat, and by sudden cooling the carbon combines with the iron to a homogeneous metallic mass; but the polycarburet can be reproduced by heating again to a red heat, and then slowly cooling.

Karsten further shows that the constitution of the polycarburets from the outer and inner mass of the iron is different, and is due to the longer continued action of the high temperature upon the inner portion of the iron; also that this difference shows the effort made by the carbon to free itself from the iron.

Grey pig with 7·1839 specific gravity, and 4·028 total carbon was melted and poured into a thick iron basin. A portion of the outer rim of the mass had a specific gravity of 7·5467 and 5·0929 per cent. combined carbon; the inner kernel, 7·1753 specific gravity, and 3·8047 per cent. total carbon, whereof 3·1941 per cent. was graphite, and 0·6106 per cent. chemically combined.

The analogy between grey pig and steel is thus evidenced. In the sudden cooling it is considered that a great force is developed, tending to press together the separated molecules. By this, it is not inevitable that the hardened steel should become denser; in fact, the specific gravity sinks with the increase of hardness. It is, therefore, held that the sudden cooling fixes in their place the molecules driven asunder by the power of the heat, the force set free being unable to overcome the rigidity of the mass induced by the sudden cooling.

This sudden force and its effect upon the combination of the carbon in the iron can be produced by other means also, viz., by the blow of a heavy hammer, or by a great pressure under the roller.

W. S.

Mushet's Steel. By F. Gunner (Dingl. polyt. J., ccvii, 316—321).

This steel, manufactured by the "Titanic Forest Steel Works Company," is so hard that ordinary steel may be cut with it; it can be worked at a low red heat; if plunged into water while hot it breaks into small pieces; it may, however, be tempered by slow cooling in an oil-bath.

This steel, according to the author, contains no titanium, but about 8 per cent. of tungsten, associated with ·014 per cent. carbon, and ·0024 per cent. silicon. A full analysis is not given.

M. M. P. M.

Copper-plating of Cast-iron, Malleable Iron and Steel.
By O. Gaudoin (Dingl. polyt. J., ccviii, 50).

1. The articles are dipped into a bath of molten copper, over which is a layer of powdered cryolite and phosphoric acid.

2. The articles are immersed in a molten mixture of cuprous chloride or fluoride with 5 or 6 parts cryolite, together with a little barium chloride (which renders the mixture more fusible) contained in carbon crucible.

3. A solution of 1 per cent. copper oxalate with a large excess of potassium binoxalate in 10 to 15 parts of water is made, and into this the thoroughly cleansed articles are dipped.

By the employment of an electric current in processes (2) and (3) a better result is obtained.

M. M. P. M.

Tinning, &c., of Brass, Copper, Iron, &c., in the Wet Way.
By C. Paul (Dingl. polyt. J., ccviii, 47—49).

The zinc or iron articles are immersed in a mixture of 1 part sulphuric or nitric acid with 10 parts water; a solution of copper sulphate or acetate is then slowly added. After the deposition of a thin layer of copper, the articles are removed, washed, moistened with a solution of 1 part "tin crystals" in 2 parts water and 2 parts hydrochloric acid, and then shaken up with a mixture of fine chalk and copper-ammonium sulphate, which is prepared by dissolving 1 part copper sulphate in 16 parts water and adding ammonia until a clear dark-blue liquid is obtained.

The articles may now be tinned by immersion in a solution of 1 part tin crystals with 3 parts white argol in water. Brass, copper, or nickel goods, also iron and zinc articles which have been copper-plated, may be silvered by treatment (after thorough cleansing) with a solution of 14 grams silver in 26 grams nitric acid, to which is added a solution of 120 grams potassium cyanide in 1 litre water, and also 28 grams finely-powdered chalk.

Further directions for producing shades of colour on the silvered articles are given in the original paper.

M. M. P. M.

On the Roasting of Pyrites.

By F. BODE (Dingl. polyt. J., ccviii, 76).

A COMPARISON of the merits of certain forms of furnace for roasting pyrites.

W. S.

Improvement in obtaining Hydrocarbons. By J. YOUNG. Patented 28th February, 1872. (Dingl. polyt. J., ccviii, 78.)

IN order to obtain, in the distillation of coal, bitumen, &c., a greater yield of oils, the condensers in which the least volatile products are intercepted, are combined with a system of perpendicular pipes or shafts, filled with coke, down which paraffin oil is allowed to flow. The vapours escaping condensation in the condensers are absorbed by the paraffin oil.

W. S.

An Improved Process for Preparing Anthracene.

By F. VERSMANN (Dingl. polyt. J., ccvii, 72—76).

INSTEAD of stopping the distillation of the tar at the point where only pitch remains in the retort, the operation is driven to the end, so that a dense coke is all that remains. In this way it is found that about two per cent. of anthracene is obtained from the tar instead of half a per cent. The dead oil is separated from the distillate by great pressure, and the pulverised residue is washed with petroleum spirit (b. p. 70°—90° C.) and again pressed. The process is patented in England and the United States.

C. H. G.

Manufacture of Caoutchouc.

By P. HASENCLEVER (Dingl. polyt. J., ccvii, 174).

THE author's experiments showed that 40 to 50 per cent. of mineral matter was contained in manufactured caoutchouc from a certain manufactory. The ordinary test for the good quality of caoutchouc is that its specific gravity be 0·985, and, therefore, that it floats on water. Cork and sawdust are amongst the substances used to adulterate it. The cheaper and poorer caoutchouc may be used not disadvantageously as an impervious material for connections of steam and water pipes, &c., the large quantity of admixed mineral matter being rather an advantage than otherwise. Caoutchouc after long standing in the air becomes very hard.

W. S.

Preparation of Red Quick-matches of Gun-cotton.

By R. BOETTGER (Chem. Centr., 1873, 107).

COTTON is somewhat loosely worked into perfectly dry cords, which are introduced into nitric acid of ordinary commercial strength contained in a stoneware vessel, so that the cotton is completely soaked and

penetrated by the acid. After this the acid is poured off from the cotton, and this is freed as much as possible from adhering acid by squeezing, &c. The cotton twists are now placed in a perfectly cold mixture of two measures of concentrated sulphuric acid of 1·84 sp. gr. and one measure of concentrated nitric acid of 1·5 sp. gr., so that the material is quite covered by the acid. It is kept in this mixture for twenty-four hours. The vessel in which this operation is carried on may be of stoneware or, better, of cast-iron. During the operation of steeping, the vessel is kept closed. The cotton is now removed from the acid, pressed from adhering acid, placed in a vessel containing a tolerably strong solution of potash or soda, and kept there till no more traces of liberated carbon dioxide escape. It is finally washed well with water until the washings are neutral to test-paper, and then moistened with alcohol and again wrung out, when it is placed in an alcoholic solution of fuchsine, and then washed with water to remove any colour not absorbed by the fibre. The cotton is dried at a temperature not exceeding 50° to 60° R., best in a current of warm air.

W. S.

Raw Sugar of the Third Produce and the Commercial Analysis of the same. By C. Viollette (Compt. rend., lxxvi, 642—645).

Molasses exceptionally rich in potassium chloride under some conditions furnish sugars containing notable quantities of sucrate of potassium chloride, $C_{12}H_{20}O_{11}.KCl$. A sample from the third crystallisation, from Limagne in Auvergne, contained 36 per cent. of this substance, which, being isomorphous with cane-sugar, cannot be detected by the appearance of the sugar. The commercial estimation of the ash of sugars by incineration, with addition of sulphuric acid, and the deduction of one-tenth the weight of the residue, gives too high results.

The ash of these sugars of the north of France represents very closely three-fourths the weight of the salts existing in the sugar.

E. K.

Manufacture of Acetic Acid. By Buchem (N. Repert. Pharm., xxii, 168).

The author refers to Dobereiner's oxidation of alcohol by platinum black, and to the circumstance that no *Mycoderma Aceti* was to be found in the contents of a vat for oxidation of alcohol by air, which had been in use for 25 years, in order to prove that the conversion of alcohol into acetic acid is brought about only by the action of oxygen. The vinegar plant and allied substances probably act in the same way as platinum black.

C. R. A. W.

Free Acids in Wine. By Graeger (Dingl. polyt. J., ccvii, 430).

The processes of wine-making of Dr. Gall and of Petiot, in which the must is diluted with water, cause the introduction of free sulphuric

and hydrochloric acids into the wine, if the water used contains calcium sulphate or chloride, from double decomposition of these salts and potassium bitartrate. These acids, more especially the hydrochloric, give the wine a disagreeable taste. Care should therefore be taken to use water as free as possible from these salts, and the author further recommends the use of malic acid in place of tartaric in Petiot's process, for the purpose of raising the acidity to the normal standard.

The process of "plastering" the grapes pursued in some districts introduces considerable quantities of free sulphuric acid into the wine.

E. K.

Specific Gravity of Cork. By W. Rollmann (Dingl. polyt. J., ccvii, 431).

Corks, as far as possible perfect, gave the numbers ·12, ·15, ·18, and ·195.

E. K.

Pasteur's New Process for Brewing. (Dingl. polyt. J., ccvii, 175.)

The wort after boiling in the brewing-pan is run into closed vessels, from which all air is driven out and excluded by a stream of carbon dioxide. The vessels are at the same time cooled down, and the fermentation thus allowed to proceed with exclusion of air and in the cold.

W. S.

Zinc Beer Coolers. By H. Vohl (Dingl. polyt. J., ccvii, 511).

Two samples of beer from the same brewery, and made by exactly the same process, were submitted to the author for examination, the one which had been cooled in the old zinc cooler being bright and clear, whereas the other, which had passed through a new zinc cooler, was faintly opalescent. Both samples had a pure and fresh taste, but the second one was objectionable on account of its slight turbidity.

On analysis the first sample was found free from foreign matter, whereas the second contained a trace of zinc oxide, but how this trace of zinc could cause the turbidity is difficult to say. The composition of the metallic plates of the coolers was, however, found to be different, that of the one from which the first sample of beer was taken being zinc 99·43, and lead 0·44 p. c., whilst that of the one from which the second was taken was zinc 98·64 and lead 1·28 p. c.

It is considered not unlikely that the larger amount of lead in the latter case would exert an influence upon the solubility of the zinc.

W. S.

Bruening's New Method for Manufacturing Rosaniline. By A. Coupier (Deut. Chem. Ges. Ber., vi, 423).

Bruening has lately published a new method for manufacturing magenta (see this Journal, 1873, p. 658). This method is, however, not new, having been patented by the author in 1866.

C. S.

Dyeing Wool with Aniline Green. By C. Lauth (Bull. Soc. Chim. [2], xix, 401—403).

As aniline green, unlike most other aniline dyes, appears to possess but little affinity for wool, the author proposes to mordant it with electro-positive sulphur precipitated from a bath of sodium thiosulphate containing a little alum, by the addition of an acid; sulphur deposited from its solution in carbon disulphide, or precipitated from the poly-sulphides by an acid, cannot be used; moreover the wool, before mordanting, should be cleansed, and treated with dilute hydrochloric acid to remove any metallic salts which would otherwise give a brown shade, from formation of metallic sulphides. The wool is dyed in the usual way in a solution of the green in hot water; the shade can be rendered more or less yellow by the use of picric acid, adding to the bath at the same time some acetate of zinc or acetate of soda, accordingly as a yellow or a blue green is required. Mixed fabrics of wool and cotton can be dyed by mordanting first with sulphur and then with sumach.

C. E. G.

Flavin. By A. Ott (Dingl. polyt. J., ccvii, 322—327).

This article is almost entirely historical. The samples of flavin examined by the author contained no tannin or quercitrin, but a little gallic acid.

M. M. P. M.

Indulin Ink. (Dingl. polyt. J., ccvii, 430.)

Coupier and Collin's blue-black, known by the name of Indulin, dissolved in water in the ratio of 20 parts to 1,000 of water, forms a writing ink of a good colour, which it retains when treated with chemical agents. It does not corrode steel pens, and remains liquid. This ink is specially recommended for schools, as it can be washed out with water.

E. K.

Indestructible Colours. (Dingl. polyt. J., ccvii, 176.)

One dram of aniline black is rubbed with a mixture of sixty drops of concentrated hydrochloric acid and three-quarters of an ounce of alcohol. The deep blue solution obtained is diluted with a hot solution of one and a half drams of gum arabic in three ounces of water. This colour does not attack steel pens, and is unaffected by concen-

trated mineral acids or strong alkalies. If the aniline-black solution, instead of being diluted with gum-water, be treated with a solution of between a half and three-quarters of an ounce of shellac in three ounces of alcohol, an aniline-lake is obtained, which is remarkable for producing a very deep black colour on brass or leather.

W. S.

Preparation of Alcoholic Lakes. By A. Morell (Dingl. polyt. J., ccviii, 79).

Amongst the many spirit varnishes, the gold varnishes are especially defective in not adhering firmly enough to a metallic surface.

To remedy this, pure crystallised boric acid is dissolved in the varnish to the extent of half a part in 100 parts of the varnish. Thus improved, the varnish poured upon a plate forms a hard glassy coating, so firmly adherent and hard as to be impenetrable on scratching with the finger-nail.

The above proportion of boric acid must be carefully adhered to, or the varnish loses its intensity of colour.

W. S.

Alumina Soap as a Lake. (Dingl. polyt. J., ccvii, 173.)

This lake possesses great flexibility, and is superior to all others in being unaffected by a high temperature. Besides being applicable to all kinds of material to be rendered waterproof, this soap in solution may be used with advantage to coat metallic surfaces which have to withstand considerable heat. In the air, articles thus coated dry slowly; if exposed to a temperature of 50°, more quickly. To prepare the soap, a solution of alum or aluminium sulphate is added to a dilute boiling solution of soap, so long as a separation of white hydrated alumina soap takes place. The white precipitate is washed with hot water to remove adhering saline solution, and is heated to remove water. By these means a transparent soap is obtained resembling glycerin soap, soluble in warm oil of turpentine in all proportions. The water may also be driven off by heating with oil of turpentine. When the solution becomes thick and transparent, the lake is ready. For making this alumina soap a good yellow rosin soap is the best to use.

W. S.

Polishing Paste for Wooden Furniture. (Dingl. polyt. J., ccvii, 174.)

Eight parts of white wax, two parts of rosin, and half a part of Venice turpentine, are melted at a gentle heat. The warm mass, completely melted, is poured into a stone jar, agitated, and six parts of rectified oil of turpentine are added thereto. After 24 hours, the mass having the consistency of soft butter, is ready for use. Before using the paste, the furniture should be washed with soap and water, and then well dried.

W. S.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XXXVII.—*Researches on the Action of the Copper-Zinc Couple on Organic Bodies.*

Part III. *On Normal and Iso-Propyl Iodides.*

By J. H. GLADSTONE, Ph.D., F.R.S., and ALFRED TRIBE, F.C.S.

As the iodides of ethyl and of amyl are decomposed by our copper-zinc couple at a temperature below their respective boiling points, we anticipated that the same would be the case with the intermediate iodides of propyl and butyl. As these bodies offer to us isomeric modifications, an additional point of interest was included in their investigation.

In the present paper we confine ourselves to the propyl compounds, but hope at some future time to describe the reactions with all the butyl iodides, if we are fortunate enough to procure specimens of them.

Action of the Dry Couple on Isopropyl Iodide.

The isopropyl compound, being the more accessible body, was the first examined. Our specimen had a constant boiling point, and seemed perfectly pure.

If it be heated to 50° with a dry copper-zinc couple a faint cloud appears in the flask after the lapse of some minutes, and gases are evolved. The action proceeds rapidly, and no further change takes place even at a boiling temperature.

In one experiment 5 c.c. (8·73 grms.) showed signs of action in fifteen minutes, and during the next four minutes 453 c.c. of gas were collected and the action ceased, leaving in the flask a body liquid at the ordinary temperature and a solid (probably iodide of zinc) which it held mainly in solution. When air was admitted to the flask white fumes formed in the neighbourhood of the liquid. When this was gently heated over a gas flame 424 c.c. of gas were quickly evolved and a small quantity of a liquid distilled. This liquid fumed in the air, and on decomposition by water gave 0·068 zinc oxide, which would be equivalent to 0·127 grm. of zinc-propyl.

In another experiment with the same quantity of isopropyl iodide at 50° the action commenced in twelve minutes, lasted six minutes, and yielded 425 c.c. of gas. The flask was then heated to 100° and kept at that temperature for twenty minutes, but no gas was evolved. It was then raised 132° and maintained at 132°—138° for two hours

During the whole of this time gas was slowly evolved, amounting to 283·2 c.c., while a little liquid distilled. The temperature was then increased, and 81·6 c.c. of gas and a further trace of liquid were obtained. The total gas collected was therefore 789·8 c.c. The amount of zinc-oxide formed by the decomposition of the two small portions of liquid in the tubes and receivers was ·018. The amount of liquid in the receiver was certainly more than ·033 grm., leading us to the belief that a little dipropyl (C_6H_{14}) is formed, as there was no iodide.

As in the course of our experiments on amylic iodide (p. 678 of this volume) we found more zinc-amyl produced when the contents of the flask were heated *in vacuo*, we adopted the same plan in this instance also.

Another preparation was made at 50° and it was then heated to 132° while the gas was constantly being pumped out. A good deal was given off, but also a much larger quantity of the liquid body than in the previous experiments. On the admission of air to the receiver this liquid was suddenly changed into a light brown solid, with evolution of much heat. On addition of water it was decomposed with a crackling noise. The oxide of zinc was ·544, which, if the liquid were zinc-propyl, would indicate 1·01 grm. of that body prepared from 8·7 grms. of the iodide.

The gas given off during the reaction at 50° was analysed by Bunsen's method, after it had been passed through a set of bulbs containing respectively alcohol and water. When it was treated with Nordhausen sulphuric acid the following data were obtained from two different preparations:—

	Volume observed	Temperature.	Difference of Hg. level.	Barometer.	Vol. at 0° C. and 1 m.
I. Gas used (dry)	65·57	18·2	95	750 06	40·51
After treatment (dry)..	34·85	13·5	101·8	758 19	22·11
II. Gas used (dry)	165·1	8·8	98	756 66	118·14
After treatment (dry)..	95·7	9 3	82·8	756 66	62·69

It appears therefore that the gas capable of being absorbed was per 100 volumes—

Expt. I.	Expt. II.	Mean.
45·43 vols.	44·55 vols.	44·99 vols.

A portion of the gas not absorbed by sulphuric acid was exploded in the usual way, and the following are the results:—

	Volume observed.	Temperature.	Difference of Hg. level.	Barometer.	Vol. at 0° C. and 1 m.
I. Gas used (moist)	27·15	14	422	763·78	8·68
After adding air and O (moist)	284 39	14	165·8	763·78	158·83
After combustion (moist)	251·47	14·5	199	763·78	132·19
After absorption of CO_2 (dry)	213·14	16 7	220·5	749 81	106·57

This gives the following results, which are compared with those calculated for hydride of propyl:—

	Found.	C_3H_8.
Gas burnt	8·68	—
Contraction	26·64	26·04
Carbonic anhydride	25·62	26·04

Another combustion gave nearly the calculated amount of carbonic anhydride, but the first contraction exceeded still more what was expected. The interior of the eudiometer, however, after the explosion presented an appearance which led us to think that some combination of oxygen with nitrogen had taken place. This of course would account for an excess of contraction.

Some of the gas which had not been treated with sulphuric acid was burnt.

	Volume observed.	Temperature.	Difference of Hg. level.	Barometer.	Vol. at 0° C. and 1 m.
Gas used (moist)	22·57	11	416·2	746·76	7·11
After adding air and O (moist)	284·49	10	157·7	746·51	159·36
After combustion (moist)..	258·82	9 2	180·8	745·1	139·61
After absorption of CO_2 (dry)	225·04	9·3	217	756·66	117·67

Now if we assume that 100 volumes of this gas contain 45 volumes of propylene, as we are warranted to do by previous experiments, the 7·11 vols. may be supposed to be made up of 3·2 vols. of propylene, C_3H_6, and 3·91 vols. of hydride of propyl, C_3H_8. Calculating from this, we obtain numbers very similar to those found—

	Found.	Calculated.
Gas employed	7·11	—
Contraction	19·75	19·73
Carbonic anhydride	21·94	21·33

It may therefore be concluded that the gas evolved at 50° is a mixture consisting of nearly equal volumes of C_3H_6 and C_3H_8.

The gas evolved in the second part of the operation was also examined. The amount collected when the contents of the flask were submitted to dry distillation was rather less, as already shown, than that collected during the reaction at 50°, and when treated with Nordhausen sulphuric acid it was found to contain about half its volume of an olefine. It would appear therefore that the gas given off in the two parts of the reaction is of essentially the same composition, and the probable reaction is as follows:—

$$\begin{cases} Zn + 2C_3H_7I = ZnI_2 + C_3H_6 + C_3H_8 \\ 2Zn + 2C_3H_7I = ZnI_2 + Zn(C_3H_7)_2. \end{cases}$$

The two reactions go on simultaneously in about equal proportions at 50°.

$$Zn(C_3H_7)_2 \text{ heated to } 132° = Zn + C_3H_6 + C_3H_8.$$

Action of the Couple on Isopropyl Iodide and Water.

It was found that this iodide, like those previously examined, is decomposed at the ordinary temperature by the couple wet with water. The action commences at once.

In the first experiment with 5 c.c. of the iodide, gas was slowly evolved for 48 hours, the temperature varying from 7° to 11°. The amount collected was 820 c.c.

In another experiment, where the temperature was 13°—16°, 831 c.c. were collected in 40 hours.

The gas thus produced was found to be readily soluble in alcohol and to burn with a luminous flame. Two portions treated with Nordhausen sulphuric acid gave an absorption amounting respectively to 7·93 and 9·73 per cent.

After removal of the residuary gas of one of these portions to the endiometer the following data were obtained:—

	Volume observed.	Temperature.	Difference of Hg. level.	Barometer.	Vol. at 0° and 1 m.
Gas used (moist)	27·85	12	413	773·43	9·5
After adding air and O (moist)	416·6	6·2	28	754·07	293·3
After combustion (moist)	388·3	6·2	50·6	754·38	264·65
After absorption of CO_2 (dry)	368·6	9	74·6	735·84	236·28

which gives the following results, agreeing very closely with those calculated for propyl hydride:—

	Found.	C_3H_8.
Gas used	9·5	—
Contraction	28·65	28·5
Carbonic anhydride	28·37	28·5

Action of the Couple on Isopropyl Iodide and Alcohol.

The action of this iodide with alcohol was more rapid than with water, as was also the case with the iodides previously examined.

5 c.c. mixed with 10 c.c. of absolute alcohol were poured upon the dry couple, at a temperature of 9°. In four minutes there was an evolution of gas, which proceeded so rapidly that the flask had to be immersed in cold water, at 7°. Nevertheless in four more minutes the action was complete, and 823 c.c. of gas had been collected. In another experiment 5 c.c. of the iodide were poured upon a couple which had been washed with absolute alcohol, but not dried. The temperature was 17°. Evolution of gas commenced in two minutes, when the flask was at once immersed in water at 13°. In ten minutes, 885 c.c. had been collected. The whole gas evolved in this experiment was 913 c.c.

If the propyl contained in 5 c.c. of the iodide were wholly converted into C_3H_8, it should yield 1150 c.c. of gas. The actual yield, therefore, whether in the case of water or alcohol, is considerably less than the theoretical, but this probably arises from its solubility in the water over which it was collected, and the carrying over of some vapour of the iodide.

Action of Zinc alone.

As isopropyl iodide is so easily decomposed by the copper-zinc couple, it occurred to us that it might be attacked by zinc alone. On trying the experiment with clean zinc foil it was found that no action whatever took place at 50°, though the heat was continued for an hour, but that on immersing the flask in boiling water, evolution of gas commenced in eight minutes, and proceeded so rapidly, that in twelve minutes more it was complete, and 605 c.c. of gas had been collected. The residue in the flask fumed slightly in the air, and when heated gently over a flame, it gave off 177 c.c. of gas, and a small quantity of the volatile zinc compound decomposible by water.

For the purpose of comparison, a flask containing 5 c.c. of the iodide, and the ordinary copper zinc couple was similarly immersed in boiling water. Evolution of gas commenced at once, and in five minutes the action was complete, 490 c.c. of gas being collected.

This illustrates the fact that even when zinc alone is capable of effecting a decomposition, the copper-zinc does it at a lower temperature, or with greater rapidity; also that the decomposition is not

identical in the two cases, for the more elevated temperature causes a larger proportion of the organic compound to be resolved into hydride and olefine.

On repeating the above experiment with pure zinc, finely granulated, we found that with it also the reaction took place at the boiling temperature.*

The reaction with isopropyl iodide and water and clean zinc takes place exceedingly slowly at 20°; when the usual quantities were employed, only 35 c.c. of gas were collected in 24 hours. When the temperature is raised, the production of gas is greatly increased.

The reaction with the iodide and alcohol with clean zinc foil at 20°, commenced in a few minutes, and the action proceeded rapidly, but not so violently as with the couple. With pure zinc granulated, we obtained the same result.

Propyl hydride has been prepared by Schorlemmer (*Proc. Roy. Soc.*, 1869, p. 373) by the mutual action of isopropyl iodide, zinc, hydrochloric acid and water, but the reaction with zinc alone in presence of alcohol, seems to offer a better method of preparing this gas; better, in fact, than when the couple is employed, as it is more manageable.

Action of the Dry Couple on Normal Propyl Iodide.

We procured a specimen of the normal propyl iodide, which boiled almost constantly at 101°, and we found that it was attacked very slowly by clean zinc foil, or pure zinc, even at its boiling point, and that it was acted on by the couple very differently from the iso-compound.

In the first place 5 c.c. (8·81 grms.) were heated in contact with the dry couple for an hour at 50°, the temperature at which the iso-compound is attacked, but no action whatever took place. A similar portion was afterwards heated with the couple, at 80°, in the manner described in a previous paper (*Chem. Soc. Journal*, May, 1873, p. 445). In forty minutes dense white fumes were observed in the flask, but they were not accompanied by any appreciable evolution of gas. The heating was continued for twenty minutes, when the flask was allowed to cool, and its contents were washed out with ether. When water was added to this solution, a brisk effervescence ensued, and hydrated oxide of zinc was thrown down. The amount of zinc-oxide was 1·414, which would be equivalent to 2·636 grms. of zinc-propyl, and that would be 67·4 per cent. of the amount theoretically obtainable from 5 c.c. of the iodide.

* This reaction is the more remarkable, as Schorlemmer finds that isopropyl iodide is not decomposed by sodium, even at the boiling-point. See *Proc. Roy. Soc.*, 1867, p. 34.

In a subsequent experiment the same quantity of iodide was heated in contact with the dry couple, by means of a chloride of calcium bath at 109°. At the end of ten minutes the return flow of the liquid appeared to have ceased, while very little gas—not more than 50 c.c.—had been evolved. When cool, the organic compound in the flask did not crystallise, but seemed, as in the case of the iso-compound, to be a liquid body, holding a solid in solution. It was distilled in a current of carbonic gas, in the same way as the ethyl compound had been distilled, and a liquid came over, which, when decomposed by water, yielded 1·32 gram of ZnO, equivalent to 2·46 grams of zinc-propyl, or 62·9 per cent. of the possible amount. Yet the distillate contained some undecomposed propyl iodide.

The experiment was repeated with this difference, that after the return flow had ceased, which required nine minutes, the flask was exposed for another nine minutes to the heat of a bath at 117°. The product was liquid, as before, but the distillate contained no iodide, and yielded 1·578 ZnO, equivalent to 2·94 grams of zinc-propyl, or 75·2 per cent. of the possible quantity—a larger yield than we ever obtained in the case of zinc-ethyl.

A third experiment was made with a specimen of the normal propyl iodide obtained from another source. The result was as before; but the liquid product was distilled into a weighed receiver, previously filled with carbonic acid, and was found to weigh 2·712 grams, or 69·3 per cent. of the theoretical amount of zinc-propyl, obtainable from 5 c.c. of iodide employed. On re-distillation, the great bulk came over between 146° and 148°.

A preparation was then made on a larger scale, 15 c.c. of the iodide were taken, and three times the usual amount of couple, a two-ounce flask being still employed.* When it was heated in a bath at 109°, the return flow ceased in thirteen minutes, but a temperature of 117° was maintained for twenty minutes more, in order to insure complete conversion. There was some gas evolved during the whole period, but the production diminished considerably towards the end. The quantity collected was 290 c.c. When the bath was heated at 149° distillation commenced, but it was finished off at 182°. The flask then contained some reduced zinc, partly in a crystalline form. The liquid in the receiver weighed 8·563 grams, or 73 per cent. of the possible amount of zinc-propyl. On re-distillation in a bath, the whole passed over between 142°—148°, leaving a small residue of metallic zinc.

Zinc-propyl thus produced is probably the same body as that which Cahours obtained by double decomposition, though that chemist has

* Two-thirds of the couple was transferred from another flask in which it had been prepared, dried, and annealed.

not yet published a description of it. Our compound is a colourless mobile and volatile liquid, of specific gravity 1·098 at 15° C., and boiling at about 146°. When exposed to the air it takes fire spontaneously,* burning with a bluish white flame. If dry air be allowed gradual access to it, it is converted into a white solid, which does not fume in contact with air, but is decomposed by water, with a crackling noise and effervescence.

1·0885 grm. of the liquid yielded on decomposition with water, 0·583 grm. ZnO, giving the following percentages:—

	Found.	Calculated for $Zn\left\{\begin{matrix}C_3H_7\\C_3H_7\end{matrix}\right.$
Zinc..........	42·98	43·04

Action of the Couple on Normal Propyl Iodide and Water, or Alcohol.

When 5 c.c. of the normal iodide were poured upon the couple wet with water at 13°, gas was almost immediately evolved, but the action proceeded very slowly. In about 84 hours it ceased, when 884 c.c. were found in the receiver. The temperature had varied from 13° to 19°. This gas was not diminished in volume by treatment with Nordhausen sulphuric acid; it dissolved readily in alcohol, and burnt with a very luminous flame.

When 5 c.c. of the normal iodide were poured upon the couple wet with absolute alcohol at 15°, evolution of gas commenced in twenty minutes, soon after which the temperature of the flask rose considerably. The action was complete in 45 minutes, when 766 c.c. had been collected, but some iodide had distilled over unchanged.

In another similar experiment the action commenced in 28 minutes, when the flask was at once immersed in water at 17°. Gas was evolved for about 24 hours, when 868 c.c. had been collected.

The amount of gas, as usual, falls short of the quantity possible on the supposition that the propyl passes over entirely as the hydride, C_3H_8, viz., 1161 c. c., but it shows at least that the gas obtained corresponded to 2 volumes.

Comparison of Results.

This inquiry has added to the evidence already existing of the comparative instability of the iso-propyl compounds. We have noticed the following points of contrast:—

The iso-propyl iodide is rapidly decomposed by zinc alone at its boiling point, 89°, while the normal propyl iodide is decomposed very slowly by zinc alone at its higher boiling point 101°.

* It was found that zinc-propyl was rendered not spontaneously inflammable by admixture with a little less than 3 per cent. of propyl iodide.

The iso-compound is decomposed by the copper-zinc couple at about 50°; the normal compound at about 80°.

In this decomposition about half of the iso-compound is split up into permanent gases; little, if any, of the normal compound is so split up.

The resulting liquid in the one case (zinc-isopropyl?) is scarcely volatile; that in the other case (zinc-propyl) rises easily in vapour, notwithstanding its high boiling point. The first is decomposed at about 132°, giving mainly gases and metallic zinc: the second distils over unchanged at a higher temperature.

The reaction between the propyl iodide and water, or alcohol, with the couple, takes place much more rapidly in the case of the iso-compound than in that of the normal compound; while an olefine makes its appearance during the decomposition of the first, but not of the second.

On comparing these results with those previously obtained with the ethyl and amyl compounds, it is evident that it is the normal, and not the iso-propyliodide that is acted upon in an analogous manner. The main difference perhaps is that there seems to be no crystalline propyl-iodide of zinc, but that the reaction is mainly, if not wholly—

$$2C_3H_7I + 2Zn = ZnI_2 + Zn(C_3H_7)_2.$$

Additional Notes on the Couple.

In performing these experiments with 5 c.c. of liquid, we have employed zinc foil having a surface of about 260 square centimeters on each side and weighing about 9 grams. It is crumpled up and torn to pieces just so as to introduce it into the flask, and leave irregular spaces between the different pieces. After treatment with copper sulphate, the zinc sulphate produced should be thoroughly washed away; and particular attention should, of course, be paid to the purity of the alcohol and ether with which it is dried, for any deposit on the surface would be highly injurious. In drying the couple in a stream of carbonic acid it has been found convenient to heat it till the zinc begins to soften, not melt; on cooling, the zinc will be found to be annealed, and may be gently pressed to the bottom of the flask.

It has been suggested to us that zinc foil necessarily contains some quantity of lead, and that this may have an important bearing on the reaction. Specimens of zinc from various sources have, therefore, been examined, and have given the following percentages of lead:—

Zinc foil used for couple*	0·96 and 0·93 per cent.
Granulated zinc, commonly used in our laboratory..............................	1·13 per cent.

* Supplied by Messrs. Hopkin and Williams.

Granulated zinc from Dr. Frankland's laboratory	0·96 per cent.
Ordinary sheet zinc	0·89 „

It appears, therefore, that the zinc foil contains no more lead than the form of zinc which has been usually employed, and we have no evidence to show whether the presence of one per cent. of this metal is favourable or unfavourable to the action of the couple.

A comparative experiment was made with 18 grams of granulated zinc on which copper had been deposited in the same manner as before. It gave with normal propyl iodide the same reaction as the couple made of foil, but much more slowly. This superiority of the foil depends doubtless on its presenting so large an extent of surface in a given cubical space, and therefore forming so large a number of small circuits between the two metals and the liquid.

XXXVIII.—*On Cymene from Different Sources Optically Considered.*

By J. H. GLADSTONE, Ph.D., F.R.S.

DR. C. R. A. WRIGHT (*Journ. Chem. Soc.*, 1873, p. 686), has lately described the preparation of cymene from different sources, and has stated that the different specimens had the same chemical properties. The following are the determinations of the specific gravity and indices of refraction of eight specimens which he placed at my disposal, all of which had boiling points between 173° and 178°:—

Source of Cymene.	Temp.	Specific gravity.	Refractive index.		
			A.	D.	H.
Cummin oil	16°	0·8569	1·4819	1·4901	1·5173
Pre-existing in turpentine	16°	0·8555	1·4775	1·4851	1·5111
„ myristicene	16°	0·8630	1·4799	1·4876	1·5145
From hesperidene dibromide, I ..	13°	0·8605	1·4835	1·4916	1·5196
„ „ II..	15·5°	0·8638	1·4831	1·4909	1·5187
From camphor by PCl_5..........	16	0·8621	1·4852	1·4935	1·5218
From myristicol by $ZnCl_2$	11·5°.	0·8124	1·4706	1·4776	1·5021
„ PCl_5	13°	0·8620	1·4815	1·4888	1·5172

From these numbers may be deduced the following optical data; the specific refractive energy and refraction equivalent being calculated for the line A, and the specific dispersion being the difference between the specific refractive energies for A and H.

Source of Cymene.	Specific Refractive Energy for A.	Specific Dispersion.	Refraction Equivalent for A.
Cummin oil	0·5623	0·0414	75·3
Pre-existing in turpentine	0·5581	0·0393	74·7
„ myristicene.......	0·5561	0·0401	74·5
From hesperidene dibromide I ..	0·5619	0·0419	75·3
„ „ „ II ..	0·5596	0·0409	75·0
From camphor by PCl_5	0·5628	0·0424	75·4
From myristicol by $ZnCl_2$	0·5586	0·0374	74·8
„ „ PCl_5	0·5596	0·0404	75·0

These numbers are practically identical; they agree in fact as closely as values derived from different specimens of the same substance usually do. The optical data for cymene may be expressed by the mean values—

Specific refractive energy	0·5599
Specific dispersion	0·0405
Refraction equivalent	75·0

The interest of this observation does not lie in the fact that a given hydrocarbon can be prepared from a number of other bodies, but in the fact that cymene—a member of the aromatic series—can be prepared from bodies which have no manifest relation to that series, and still more in the light that is thrown by that circumstance on the optical properties of carbon.

It was pointed out by me in a communication to this Society (*Journ. Chem. Soc.*, 1870, pp. 107 and 147), three years ago, that every member of the great group of aromatic hydrocarbons and their derivatives, which had been examined optically gave a refraction equivalent higher by 6 or 8 than the number deduced from the values previously assigned by Landolt and myself to carbon, hydrogen, oxygen, chlorine, &c. It was also pointed out that all these bodies had a great dispersive power. This increased retardation of the rays of light was attributed to something analogous to a change of atomicity, or more precisely to the fact that the whole of the carbon atoms were not combined with two atoms of hydrogen or one of oxygen.

Now cymene, $C_{10}H_{14}$, belongs to this group. It becomes interesting, therefore, to inquire whether cymene can be prepared from substances which do not belong to the group, and if it can, whether it always exerts the same superior retarding influence on light.

Wright's experiments, and the table given above, answer both these questions in the affirmative.

Camphor, $C_{10}H_{16}O$, is not allied chemically to the phenyl compounds, and its refraction (as determined from its solution in alcohol) indicates

only the ordinary value 5 for carbon. It has also a comparatively small specific dispersion, 0·0224. Nevertheless the cymene derived from it gives evidence that some of the carbon is changed into what may be termed a super-retardant condition, for $C_{10}H_{14}$ would otherwise have a refraction equivalent of only 68·2.

Hesperidene, the hydrocarbon from orange oil, like every other member of the isomeric group $C_{10}H_{16}$, has a refraction higher than that calculated from the ordinary values, but not so much higher as is the case with cymene and its congeners. It happens to be about the most refractive of all the essential oils examined, the addition being 4·0,* more than half that required by the phenyl group; while the specific dispersion is also intermediate, namely, 0·0330. This high refraction might be accounted for, if we supposed all these essential oils to be mixed, as some of them are, with a considerable amount of cymene; but that appears not to be the case with hesperidene, and there can certainly be no cymene in the polymeric group of the cedrenes, $C_{15}H_{24}$, which distil only at 250° or 260°, and nevertheless all exhibit the same moderate increase of refractive power. Yet Wright, by decomposing the bromine substitution compounds, has succeeded in converting not half, but the great bulk of the hesperidene into cymene, and the refraction and dispersion are exalted in the process.

Myristicol has probably a high refraction, though the specimens examined were never free from cymene and perhaps other substances. Indeed, Wright's recent researches have more than confirmed my former observations that this body is subject to change during distillation, and that it is always mixed with some amount of a hydrocarbon. I accept his formula, $C_{10}H_{16}O$, on the strength of the reactions by which the compound is split up into cymene and water, although neither his analyses nor mine agree well with either $C_{10}H_{16}O$ or $C_{10}H_{14}O$. An additional argument in favour of the high refraction of myristicol may be derived from the refraction of its polymeride, which, as it was distilled above 265°, must have been free from cymene. The following observations were made on Wright's specimens:—

Boiling point of preparation.	Temp. of expt.	Sp. gr.	Refractive indices.		
			A.	D.	H.
212 C.—218°........	24°	0·9407	1·4757	1·4822	1·5028
265° —285°........	25°	0·9966	1·4958	1·5010	1·5320

From which may be calculated the optical data—

* Both my original specimen, and that from which Wright prepared the cymene, indicate this.

Boiling point of preparation.	Specific refractive energy.	Specific dispersion.	Refraction equivalent.
212°—218°	0·5037	0·0288	76·8
265°—285°	0·4975	0·0363	75·6

Yet the difference is not great after all between 75·6 and 73·7, the refraction equivalent of $C_{10}H_{16}O$, calculated from the normal values of its constituents.

As the camphor, hesperidene, and myristicol from which these specimens of cymene were derived all rotate the plane of polarisation, it was interesting to observe whether this optical property was carried into the new products, and also whether any of the cymene pre-existent in the other oils exhibited this phenomenon. It was found not to be the case in any instance; the cymenes were all without action on the polarised ray.

Nevertheless, it should be borne in mind that this property of circular polarisation does not seem to depend in any way upon ultimate composition, but upon some peculiarity of internal structure; and the fact that two substances are isomeric or polymeric is no ground whatever for expecting that they should affect the plane of polarisation similarly.

The phenomena of refraction, on the other hand, are profoundly connected with the ultimate composition of bodies, and the observations recorded above seem to afford additional evidence that the super-retardant power of such compounds as cymene arises from some of the carbon atoms being combined with less than two atoms of hydrogen, or an equivalent amount of some other element or group of elements.

XXXIX.—*On the Influence of Pressure on Fermentation.*

Part II. *The Influence of Reduced Atmospheric Pressure on the Alcoholic Fermentation.*

By HORACE T. BROWN, F.C.S.

IN the first part of this paper, which I had the honour of laying before the Society some months ago, I gave a detailed account of the examination of that small proportion of gas, evolved during the progress of the alcoholic fermentation, which is not capable of being absorbed by caustic potash.

I showed also how the quantity and composition of this gas is

influenced by a reduction of atmospheric pressure, and pointed out that, *pari passu* with the decrease of pressure, there is an increased amount of acetic acid formed in the liquid, even when the presence of free oxygen is rigidly excluded.

The effect of these altered external conditions, however, upon the principal products of the fermentation, alcohol and carbonic anhydride, was not touched upon. It is to this point that I would now call your attention. I wish, however, before entering upon the main subject of this part of my paper, to refer to my notice of the discovery of nitrogen amongst the gaseous products of the alcoholic fermentation of liquids rich in soluble albuminoids. This fact, I now find, had been previously noticed by Pasteur (*Ann. Chim. Phys.*, xlviii) during the industrial fermentation of beet-root juice. He, however, referred the origin of the nitrogen to the ammonia-salts which the fresh juice of the beet contains in considerable quantities. My reasons for attributing the evolution of nitrogen to the decomposition of albuminoids I have already given.

Since the experiments I am about to describe, on the production of alcohol and carbonic anhydride under varying conditions of pressure, are for the most part comparative, it is necessary at the outset to show how nearly concordant results can be obtained by fermenting different portions of the same liquid in separate vessels, but with the same proportion of yeast, and under as nearly similar conditions of temperature, exposure to light, &c., as it is possible to place them in. In order to determine the limits of experimental error in such cases, portions of malt-wort were taken, well mixed with a small portion of yeast, and quickly divided into several equal parts, each part being fermented in a separate flask, but all being exposed, as nearly as possible, to similar external influences. The following results were obtained in two series of experiments:—

TABLE I.

Percentage (by weight) of Alcohol Produced.

	Series I.	Series II.
A..........	4·598	2·322
B..........	4·637	2·390
C..........	4·637	2·310
D..........	4·605	2·256

The fermentations of series I were conducted at a mean temperature of 15·5°; those of series II at 12·5°. In neither case was the primary fermentation finished when the distillations were made.

We see, from the results tabulated above, that in experiments of

this kind, when care is taken to preserve identity of conditions, a very close conformity in results is rendered possible.

Having settled this important preliminary, it will be desirable to give an account of the method adopted to carry out the experiments I am about to describe.

The liquid to be fermented, whether malt-wort or a solution of cane-sugar, was carefully prepared, boiled for a short time, and quickly cooled After its specific gravity had been determined, it was well mixed with a small and known quantity of yeast. A correction for the alcohol thus added was made at the end of the experiment, the alcohol in the yeast being determined in a separate and much larger portion.

The state of purity of the yeast was, in most cases, previously ascertained by a microscopical examination.* Equal portions of the liquid of about 100 c.c. each were quickly weighed out, or measured off. The portion to be fermented under ordinary atmospheric pressure was placed in a light glass flask of about 200 c.c. capacity. This flask was connected with a U-tube containing calcium chloride, or pumice moistened with sulphuric acid. The carbonic anhydride evolved from this portion was always estimated by the loss in weight of the apparatus at the close of the experiment, the excess of the gas being slowly extracted from its solution in the liquid by means of the Sprengel pump. Hydrogen was passed into the flask at the commencement to drive out atmospheric air.

When the relative proportions of alcohol and carbonic anhydride have to be determined, I believe this method gives far more accurate results than those obtainable by measuring the carbonic anhydride evolved, and calculating the amount of gas remaining in solution from an assumed co-efficient of absorption for the liquid. This latter method, which was the one adopted by Pasteur, is scarcely applicable to the fermentation of a larger quantity of sugar than would furnish ·8 or ·9 gram of alcohol or carbonic anhydride, so that an error of eight or nine milligrams in the determination of either of these products would vitiate the results to the extent of one per cent. By the method I have here adopted, from 5 to 6 grams of

* I may here state that the very purest yeast never consists exclusively of the cells of *Saccharomyces Cerevisiæ.* Careful microscopical examination with a power of not less than 500 diameters will *always* reveal the presence of a few cells of the lactic or butyric ferment, *Bacillus subtilis* (Cohn). As long, however, as the special conditions favourable to the production of the lactic fermentation are absent, these cells do not materially increase in number. In the many hundreds of specimens of yeast examined by me, I have never met with a single one in which these organisms could not be detected by a careful search. As a rule the somewhat spent yeast proceeding from the fermentation of a sugar solution, contains fewer cells of the Bacillus than the more active yeast produced during the fermentation of a liquid rich in soluble albuminoids, *e.g.*, malt-wort.

alcohol and carbonic anhydride can be readily determined, whilst an error of five or six milligrams in the final weighings would amount to only *one-tenth per cent.* I believe my determinations of the carbonic anhydride to be within ·1 per cent. of the true amount, a close approximation to exactness in experiments of this kind.

The second part of the liquid, which was to be fermented under conditions of reduced pressure, was introduced into a flask similar to that figured in Part I of this paper. The lateral tube was connected through a U-tube, filled with fragments of pumice moistened with sulphuric acid, with a second U-tube containing fragments of caustic potash and granular soda-lime. The soda-lime was found necessary to prevent occasional stoppages in the tube. This absorption-tube was connected with a Sprengel mercury pump, and was carefully weighed before being attached to the apparatus, also again at the close of the experiment, the carbonic anhydride in this case being estimated directly. All joints of the apparatus were a combination of caoutchouc and mercury, accidental loss of mercury being guarded against by a layer of paraffin. The atmospheric pressure within the flask having been reduced to the required point, the fermentation was allowed to proceed, the two flasks being placed in juxtaposition so as to be equally affected by changes of temperature.

The alcohol was in both cases estimated by distilling the neutralised liquids, after washing out the drying tubes, and by carefully ascertaining the specific gravity of the distillate made up to a certain volume The actual amounts of alcohol produced were obtained by calculation from Drinkwater's tables as given by Dupré and Thudichum in their work on wine.

One possible source of error had still to be eliminated from experiments conducted in the manner just described. The liquids to be fermented, after being well mixed with the yeast, contain of necessity a little air in solution. In the case of the portion fermented in an atmosphere of hydrogen at ordinary pressures, this air would only be slowly evolved during the progress of the experiment; whilst in the case of the second portion experimented upon under diminished pressure, the air in solution would be rapidly liberated when the gaseous tension above the liquid was reduced. Pasteur has shown ("Etudes sur le Vin," p. 277) that, in the very early stages of the vinous fermentation of must, the state of aëration of the liquid somewhat influences the rapidity of the reaction. It became then of importance to ascertain to what extent a total expulsion of the air from such solutions as were used in these experiments would influence the results. In order to obtain information upon this point, samples of malt-wort were taken and mixed with a small quantity of yeast, the liquids being well agitated for some time in order to promote complete saturation with

air. Each sample was then divided into two equal portions. One was allowed to ferment without further treatment in an atmosphere of hydrogen, whilst the other was first exposed *in vacuo* for some time until all air had been completely expelled, hydrogen being afterwards admitted to normal pressure. After fermentation for a definite time the following results were obtained :—

TABLE II.

Percentage of Alcohol Produced.

	Air in solution.	Air expelled.	Time of fermentation.
I....	4·390	4·378	2 days.
II ..	5·284	5·200	6 days.

The influence of dissolved air in determining the rapidity of the fermentation appears, then, to be extremely small after the first day or two.

We may now turn to the comparative results obtained by fermenting liquids under varying conditions of atmospheric pressure in the manner already described. These are shown in the following table :—

TABLE III.

	Under ordinary Pressure.			Under reduced Pressure.					
No.	Alcohol in grams.	Carbonic anhydride in grams.	Pressure in mm. mercury.	Alcohol in grams.	Carbonic anhydride in grams.	Pressure in mm. mercury.	Mean temperature ° C.	Time of fermentation.	Specific gravity of liquid.
I......	5·408	—	747	4·182	—	30	14·5°	7 days	1·0651
II	5·581	—	750	4·852	4·822	77	22·0°	3 „	1·0650
III....	5·866	—	749	4·522	—	212	20·0°	4 „	1·0650
IV	5·917	5·833	718	3·495	3·488	67	21·0°	5 „	1·0650
V.....	4·032	3·908	743	2·731	2·668	108	15·0°	4 „	1·0644
VI....	*3·343	3·223	746	2·614	2·584	190	13·5°	6 „	1·0833
VII ..	5·405	5·303	755	4·308	4·256	210	16·5°	9 „	1·0650
VIII ..	1 550	1·495	753	1·147	1·126	100	20·0°	11 „	1·0445
IX....	1·426	1·393	753	1·126	1·110	30	18·0°	9 „	1·0388
X	2·044	2·035	746	—	—	—	18·5°	7 „	1·0358
XI....	†2·597	2·548	750	—	—	—	18·0°	18 „	1·0400

* The yeast of this experiment was somewhat old, and consequently less active, than that used in the other cases. The fermentation was, however, with the exception of being somewhat slow, perfectly normal.

† 50 c.c. of the solution were here taken. The fermentation was very nearly complete.

In experiments I to VII, inclusive, malt-worts were used, whilst in experiments VIII to XI solutions of cane-sugar were employed.

A consideration of the results tabulated above inevitably points to the conclusion that diminished atmospheric pressure tends to retard in a remarkable manner the progress of the alcoholic fermentation. The amount of this retardation, however, does not appear to be directly proportional to the diminution of pressure, nor yet related to it in any simple way. Probably, however, by conducting a series of experiments upon exactly similar liquids, at the same temperature, some correlation would be observed between actual pressure and alcohol formed. The broad fact, however, remains, that under diminished pressure there is always less sugar decomposed than during an equal interval of time at the ordinary pressure of the atmosphere.

We have now to consider what quantitative relation the amount of carbonic anhydride bears to the alcohol under ordinary circumstances, and how this relation is affected when the fermentations are carried on in a rarefied atmosphere. The following numbers represent the varying proportions of carbonic anhydride found in the experiments already referred to, the amount of alcohol produced being in each case represented by the constant number 100.

TABLE IV.

CO_2 *in grams.* (*Alcohol* = 100.)

At ordinary Pressure.		At reduced Pressure.	
II	—	99·38	malt-wort.
IV	98·59	99·79	„
V	96·92	97·69	„
VI	96·41	98·85	„
VII	98·11	98·79	„
VIII..........	96·45	98·16	cane-sugar.
IX	97·68	98 57	„
X	99·55	—	„
XI	98·11	—	„

It will be seen that the amount of carbonic anhydride produced from fermentations at ordinary pressures, is, as compared with the alcohol formed, subject to a variation of about 2 per cent. Moreover, the interesting fact is revealed that diminished pressure tends to increase the relative amount of carbonic anhydride, this increase varying in the experiments cited from ·5 to 2·5 per cent. of the alcohol formed.

If the equation of Gay-Lussac—

$$C_6H_{12}O_6 = 2C_2H_6O + 2CO_2$$

were rigidly correct, every 100 parts of alcohol ought to correspond to 95·65 parts of carbonic anhydride.

Pasteur, in an experiment, the details of which are given in his classical memoir on the Alcoholic Fermentation, found that during the fermentation of about 10 grams of cane sugar, alcohol and carbonic anhydride were produced in the ratio of 100 : 96 09. The difference between this last number and that pointed out by the equation of Gay-Lussac he attributes to the simultaneous production of glycerin and succinic acid, according to the equation—

$$49C_{12}H_{22}O_{11} + 109H_2O = \underset{\text{Succinic acid.}}{24C_4H_6O_4} + \underset{\text{Glycerin.}}{144C_6H_4O_6} + 60CO_2$$

If it be true that the excess of carbonic anhydride which is always found is entirely due to the production of glycerin and succinic acid, it is evident that a reduction of atmospheric pressure favours this particular reaction.

In seeking for a sufficient cause to account for the comparatively slow progress of the alcoholic fermentation in a more or less perfect vacuum, it appeared possible that it might be found in the partial destruction of the torula cells constituting the parent yeast when they were placed under these altered external conditions. It did not seem improbable that, when pressure was reduced, the carbonic anhydride held in solution by the protoplasmic contents of the cell might be liberated with such violence as to rupture the cell-wall and arrest the vitality of the organism. To bring this to the test of experiment, portions of yeast were, on several occasions, placed under the receiver of an air-pump, and the air exhausted with considerable rapidity. In none of these cases could the slightest difference be observed when the cells were subsequently examined most carefully with the microscope. In no case was there any indication of ruptured cell-walls.

It was now necessary to ascertain whether yeast thus exposed for a time *in vacuo* is capable of decomposing sugar with as great rapidity as before such treatment. To determine this point, some fresh yeast was taken and mixed with distilled water to a thin homogeneous fluid. Two portions of this liquid were rapidly measured off before subsidence could take place, and one exposed for two or three hours under the receiver of an air-pump at a pressure but little above the tension of aqueous vapour at the time of the experiment. Each portion of yeast was afterwards mixed with equal portions of a cane-sugar solution, or of a malt-wort, and the fermentations allowed to proceed for the same length of time.

The following results were obtained in two such experiments:—

TABLE V.

Percentage of Alcohol Produced.

	Yeast not previously treated *in vacuo*.	Yeast previously treated *in vacuo*.	Nature of liquid.
I.....	4·068	4·128	Malt-wort (sp. gr. 1·0603)
II.....	4·200	4·186	Cane-sugar (sp. gr. 1·0388)

Thus we see that the functions of yeast as an alcoholic ferment are not materially modified by an exposure of some hours *in vacuo*. The only other reasonable explanation of the retarding influence of reduced pressure upon the alcoholic fermentation is that the organised ferment experiences greater difficulty in re-arranging the atoms of the sugar-molecule, owing to the changed physical condition of its environment, that, in fact, the sugar-molecule is more stable under conditions of low external pressure.

Sorby, in his Bakerian Lecture, on the "Direct Correlation of Mechanical and Chemical Forces," delivered before the Royal Society in 1863, concludes, from considerations based upon his own experiments and those of others, that it is highly probable "that pressure weakens or strengthens chemical affinity according as it acts against or in favour of the change in volume." That, in fact, when the re-arrangement of the atoms due to any reaction taking place slowly results in an increase of volume, pressure retards the chemical change, whilst the reverse holds good in those cases where there is an actual decrease in volume.

In order, then, to ascertain whether the foregoing results tend to increase confidence in the general application of Sorby's hypothesis, it became necessary to estimate the change in volume which takes place in a liquid submitted to the alcoholic fermentation. For this purpose 103·7528 grams of a solution of cane-sugar, having exactly the specific gravity 1·03601, were fermented with ·555 gram of previously washed and partially dried yeast containing 21·14 per cent. of dry matter. The specific gravity of the dry yeast determined in another portion was found to be 1·514. The solution was fermented for seven days at a mean temperature of 18·3°, and at the ordinary atmospheric pressure. The loss in weight was determined after expelling the excess of carbonic anhydride as in the other experiments, and the liquid was filtered from the yeast, which was washed, dried at 100°, and weighed. The specific gravity of the clear liquid was determined with great care, and also the alcohol produced. Assuming the specific gravity of the yeast left after the experiment not to differ

from that originally used, we have here all the data necessary for a calculation of the change of volume undergone by the liquid during fermentation. The following are the results of the experiments:—

Before fermentation—

Volume of sugar solution............	99·723 c.c.		100·161
„ water introduced with yeast	·438 „		
„ yeast used (·117 gram)....	·077 „		
Total volume	100·238 „		

After fermentation—

Volume of liquid	99·882 c.c.		99·938
„ water retained in drying tube	·056 „		
„ Yeast (·1685 gram)........	·111 „		
	100·049 „		

Thus we see a decided contraction in volume has taken place, amounting in the whole mixture to ·189 c.c., but in the liquid portions alone to ·223 c.c.

No doubt some portion of this contraction is due to the conversion of cane into invert sugar; but since at the end of the experiment there was still cane-sugar left in solution, and the total contraction that could possibly arise from an inversion of the whole of the sugar could only amount to ·189 c.c., it is evident that the transformation of sugar under the action of the alcoholic ferment is attended, when the evolved gas is left out of consideration, with a condensation of volume.

It is easy to show, on theoretical grounds, that such a contraction must take place. Let us take, as a hypothetical example, the complete fermentation of 100 c.c. of a solution of invert sugar, containing 10 grams of dry substance. Let it be supposed that at the close of the experiment, when the whole of the sugar has been fermented, there is just the same amount of yeast found as was originally used. The possibility of such a case has been fully shown by Pasteur. Now the 10 grams of invert sugar will, according to Pasteur, furnish on complete fermentation:—

Alcohol	4·846 grams.	
Glycerin	·322 „	
Succinic acid............	·061	·184.
Undetermined matter	·123	

The specific gravity of invert sugar *in solution* being 1·625, the 10 grams will occupy a space of 6·153 c.c. Glycerin was found by a

direct experiment to have a specific gravity when in solution of 1·295. The undetermined matter, including the small amount of succinic acid is assumed to have the same specific gravity in solution as the sugar from which it is produced.

The volumes before and after fermentation, in the case we have imagined, will then be represented as follows:—

Before fermentation (at 15·5° C.)—	
Volume of 10 grams invert sugar *in solution*	6·153 c.c.
After fermentation (at 15·5° C.)—	
Volume of 4·816 grams of alcohol	6·104 c.c.
" ·322 gram of glycerin	·248 "
" ·184 gram of succinic acid and undetermined matter	·113 "
	6·465 "
Contraction due to hydration of alcohol	·403 "
Total volume after fermentation	6·062 "

There will consequently be a total contraction of ·091 c.c. which amounts to 1·47 per cent. of the volume occupied by the sugar fermented when held in solution. Thus we see that both experiment and theory point to there being a decided contraction in volume during the alcoholic fermentation, a result which brings the phenomena attending this particular fermentation under reduced pressure into conformity with the law of Sorby already enunciated.

A word still remains to be said upon the remarkable increase of acetic acid, in liquids undergoing the alcoholic fermentation under reduced pressure.

I am now able to speak with greater certainty upon the origin of this acid than I was in Part I of this paper. In Exp. IX, Table III, the acetic acid present in that portion of the liquid fermented in the ordinary way was too small in quantity to be determined, whilst in the second portion of the same liquid, fermented at a pressure of 30 mm. of mercury and out of contact with free oxygen, the acetic acid amounted to ·172 gram. The ratio of the alcohol to the carbonic anhydride in this experiment was 100 : 98·57. If the acetic acid produced is assumed to have proceeded from subsequent oxidation of alcohol, this ratio becomes 100 : 88·03; an impossibility if the alcohol has been derived from the sugar according to the generally received equations. We are thus driven to the conclusion that acetic acid has been produced in this experiment directly from the sugar. It should be stated that, as far as microscopical examination could go, this

fermentation was quite normal, there being no indication, as might be expected from the absence of free oxygen, of the *Mycoderma aceti* (Saccharomyces mycoderma. Rees).

Whether the splitting up of the sugar molecule under peculiar circumstances, according to the equation—

$$C_6H_{12}O_6 = \underset{\text{Acetic acid.}}{3C_2H_4O_2}.$$

is correlative with the vital functions of the ordinary yeast-cells, I cannot at present say; but it is very certain that no specific organised ferment makes its appearance under these conditions.

It is interesting to note that the decomposition of the sugar molecule in this manner is just such a reaction as should, according to Sorby's law, be intensified by a decrease of pressure. That is to say, during the change there would be a large increase in the total volume of the liquid. One gram of invert sugar, for instance, occupies, when in solution in 100 c.c. of water, a volume of ·615 c.c., whilst the corresponding amount of acetic acid occupies, under similar circumstances, a space of about 1·09 c.c.

XL.—*On the Decomposition of Tricalcic Phosphate by Water.*

By Robert Warington.

Several chemists have remarked that when monocalcic or dicalcic phosphate is acted on by water, and especially if they are boiled with it, decomposition takes place, and the phosphate splits up into a more acid and a more basic compound. Thus, according to Boedeker, dicalcic phosphate is resolved by boiling with water into monocalcic and tricalcic phosphate. In no case, as far as I am aware, has the formation of a product more basic than tricalcic phosphate been observed. In 1866 I communicated to the Society some researches on the phosphates of calcium (*Journ. Chem. Soc.* [2], iv, 296), and I then stated that when tricalcic phosphate is boiled with water, it is itself decomposed, the solution becoming distinctly acid. It became at once evident that the observations already alluded to dealt only with the earlier stages of the action of water on the phosphate. I therefore, as soon as possible, commenced experiments to ascertain the ultimate action of water upon tricalcic phosphate; the results I now lay before the Society.

The tricalcic phosphate used in the following operations was prepared by pouring pure chloride of calcium into a very dilute solution of disodic phosphate, plus one equivalent of ammonia; the alkaline phosphate was kept in excess during the precipitation. The tricalcic phosphate produced was washed by decantation till no chlorine was found in the washings. All analyses of phosphates were made, unless the contrary is stated, by dissolving an unweighed quantity of the moist phosphate in hydrochloric acid, precipitating lime with oxalate of ammonium from an acetic acid solution, and afterwards the phosphoric acid with magnesia; the relation of lime to phosphoric acid was then calculated. As I was dealing with substances containing only lime and phosphoric acid, this method was, of course, admissible, and possessed several advantages.

First Series of Experiments.—Tricalcic phosphate, prepared as above, was analysed, a portion then placed in a flask, and boiled for two hours with distilled water. The solution obtained was distinctly, though not strongly acid; it contained very little lime, but a more considerable quantity of phosphoric acid. The residue was again boiled with a fresh supply of water for two hours; the solution obtained was far less acid than in the first instance. After decanting the solution, the residue was again boiled with fresh water; and this operation was repeated till the phosphate had been boiled for twenty-four hours, the water being changed every two hours. The residual phosphate was then analysed. The percentage results were as follows:—

	Phosphate taken.	First solution in boiling water.	Phosphate remaining after 24 hours' boiling.
Lime	54·37	25·87	56·33
Phosphoric acid..	45·63	74·13	43·67
	100·00	100·00	100·00

Tricalcic phosphate contains, theoretically, 54·19 lime, and 45·81 phosphoric acid per cent. There is not enough lime in the first solution to form monocalcic phosphate, which would contain (as metaphosphate) 28·28 per cent. The action of the boiling water has clearly been to diminish the proportion of phosphoric acid in the phosphate operated on.

Second Series of Experiments.—Another specimen of tricalcic phosphate was treated in the same manner as before, save that the water was changed every four hours, and the boiling continued for forty hours.

	Phosphate taken.	First solution in boiling water.	Phosphate remaining after 40 hours' boiling.
Lime	54·78	19 09	56 69
Phosphoric acid..	45·22	80·91	43·31
	100 00	100 00	100 00

The constitutional water of the residual phosphate was in this case determined; the phosphate dried at 100° lost 2·20 per cent. on ignition.

The results in this series are quite similar to those of the previous experiments, the decomposing action of the water being, however, pushed a little further. All the above experiments were made in 1866; the following have been recently completed.

Third Series of Experiments.—These were not very successful, owing to the distilled water containing a trace of copper, which gradually accumulated in the phosphate boiled in it. The boiling was continued for twenty hours, the water being changed every two hours; the experiment was then prematurely stopped.

	Phosphate taken.	Phosphate remaining after 20 hours' boiling.
Lime	54·95	56·09
Phosphoric acid..........	45·05	43·91
	100·00	100·00

The constitutional water in the boiled phosphate was 2·05 per cent.

According to the figures just given, the decomposition of the phosphate would seem to be less than in the previous experiments; it was, however, probably nearly as great, as in this case the lime must have been to a small extent replaced by copper.

In the present instance, the quantity of phosphoric acid contained in the first extract by boiling water, and also that in the last extract, was determined. 300 c.c. of the first solution gave ·1485 gram $2U_2O_3.P_2O_7$. If we calculate the phosphoric acid as tricalcic phosphate for the sake of comparison, we have here an apparent solubility of tricalcic phosphate of 1 in 4651 of boiling water. The amount of phosphoric acid taken up by the water would probably have been still greater, had the quantity of tricalcic phosphate operated on borne a larger proportion to the water; even this solubility is comparatively very high, being almost equal to the solubility of tricalcic phosphate in a 10 per cent. solution of chloride of ammonium. Of the last solution, obtained by boiling for two hours at the end of the twenty hours' series, 1000 c.c. gave only

·0035 gram $2U_2O_3.P_2O_7$, corresponding to a solubility of 1 of tricalcic phosphate in 657,332 of water. The insolubility here shown is greater than I should expect; I have, however, no second experiment on the subject. It is evident, from these results, that the work done by the water is nearly all effected in the earlier stages of its action.

Fourth Series of Experiments.—These experiments were made on a larger scale; the boilings were conducted in a capacious Bohemian flask. The proportion of phosphate to water was, in this case, about 4 grams to 1 litre; in the earlier experiments, the proportion of phosphate to water was rather smaller.*

After the experiment had proceeded some time, it was found that when the solutions from the later boilings were evaporated nearly to dryness in a platinum basin over a spirit lamp, they exhibited a marked alkaline reaction. This was soon traced to the glass of the flask, as, when distilled water alone was boiled in the flask for two hours, the same reaction was manifested on concentration. As it might reasonably be argued that the phosphate was partly decomposed by the alkali from the glass, an experiment was made with the same phosphate in a silver beaker covered by a porcelain dish. The results were as follows:—

	Phosphate taken.	Boiled in silver 29 hours.	Boiled in glass.		
			19 hours.	27 hours.	50 hours.
Lime	51·93	56·13	56·20	56·11	56·93
Phosphoric acid	45·07	43·57	43·80	43·56	43·07
	100·00	100·00	100·00	100·00	100·00

* An incident of the experiment seems worth recording as a word of warning to others.

I wished to ascertain the point at which the watery extract ceased to contain free acid, and to this end evaporated from time to time 100 c.c. of the decanted liquor in a platinum basin, and when concentrated to a single drop tested it with litmus paper. I found, to my surprise, that the watery extract after eighteen hours' boiling, when treated in this manner, still turned litmus paper scarlet. As a matter of precaution, I evaporated 100 c.c. of the distilled water employed, and found that it gave an equally acid residue. Some distilled water kindly supplied by Dr. Gilbert, which had been prepared with great care from rain water, also turned litmus paper scarlet when evaporated nearly to dryness in a platinum basin. A drop of chloride of barium revealed the cause of these perplexing reactions. The acid was sulphuric acid, arising from the argand gas-flame over which the basin was supported on a wire gauze. When the distilled water was evaporated over a spirit lamp, no reaction was obtained with chloride of barium, and the last drop of the concentration had only a faint acid reaction, probably due to impurities in the methylated spirit used.

It appears from these figures, that tricalcic phosphate is decomposed by water in a silver vessel as effectually as in a glass one.

The phosphate which had been boiled for 50 hours, contained 1·96 per cent. of constitutional water.

By long boiling, tricalcic phosphate loses its gelatinous character and becomes a finely divided substance, subsiding very slowly. No crystalline character was detected under the microscope. The boiled phosphate dissolves in acids less readily than tricalcic phosphate.

There is a considerable uniformity in the analyses of boiled phosphate. Omitting the third experiment in which copper was present, the mean proportion of lime to phosphoric acid in six analyses, is 56·50 : 43·50, while the determinations of constitutional water range from 1·96—2·20 per cent. Do these numbers agree with any formula?

The proportion of lime to phosphoric acid in apatite is 56·79 : 43·21; a proportion of lime not quite reached by the mean of these analyses of boiled phosphate, but falling within the extremes. Again, if the fluoride and chloride of calcium in apatite were replaced by an equivalent of hydrate of calcium, the compound would contain 1·79 per cent. of water, a quantity agreeing fairly with the amount of water found in the boiled phosphate. We are therefore led to the formula—

$$3Ca_3P_2O_8.CaOH_2O$$

as the one which agrees best with the analyses. We have, however, no certain ground for concluding that the action of boiling water finally results in the formation of such a hydrated oxygen apatite, since we do not know what the still further prolonged action of boiling water might effect. The boiled phosphates contained also, at least in some cases, a little carbonic acid. The phosphate boiled in silver contained a trace of carbonic acid, and that boiled for 50 hours in glass a much more distinct quantity; the alkali from the glass had in this case probably acted as a carrier of carbonic acid to the phosphate. An attempt was made to determine the carbonic acid in this latter phosphate by noting the loss of weight it suffered when fused with bichromate of potassium; the loss obtained was 1·40 per cent. If one equivalent of carbonic acid were added to the formula of hydrated oxygen apatite already given, the compound would contain 4·20 per cent.; this phosphate evidently, therefore, still held the greater part of its *outside* lime as hydrate. If further experiments are made upon the action of water on phosphates, they should clearly be conducted in metallic vessels, and at pressures above that of the atmosphere; the tedious character of the action at ordinary pressures, which allows room for the entrance of impurities, would probably be in this way obviated.

If we cannot certainly conclude that an oxygen apatite has in this case been formed, we have at least brought before us a reaction by

which it is extremely probable that apatite would be produced. If water containing fluorides and chlorides should act at high temperatures and pressures on tricalcic phosphate, it is readily conceivable that the removal of phosphoric acid by the water, and its replacement by chlorine and fluorine, should simultaneously occur, and apatite be thus produced in the wet way.

There is evidence that the decomposing action of water on tricalcic phosphate is not confined to boiling water, but is possessed in a lesser degree by cold water. I have prepared a great number of specimens of the pure phosphates of calcium, and have been very careful to exclude in their preparation all conditions which could give rise to an excess of lime, yet on analysis there has been found, almost without exception, an excess of lime over theory, the excess being often considerable. I attribute this to the fact that all the phosphates were washed by decantation; a plan which ensures the thorough washing of these bulky gelatinous precipitates, but at the same time subjects them to the prolonged action of large volumes of cold water.* Phosphates of theoretical composition are probably obtainable only by conducting the washing on a Bunsen's filter.

The perplexing irregularities which I have met with in attempting to determine the solubility of tricalcic phosphate in cold water are also explained if the action of water on the phosphate is really one of decomposition, and not one of normal solution. The solubilities I have found have varied from 1 in 35,000, to 1 in 110,000. Experiments strictly duplicate would give perfectly concordant results, but the solubility of different specimens of phosphate would vary, and the same specimen, when repeatedly treated with water, would give decreasing solubilities. Now, if my notion of the action of the water is correct, the amount of phosphoric acid which water will extract from tricalcic phosphate will depend on the extent to which the phosphate has been already acted on by water, and on the relative masses of the phosphate and water that are brought together, both which conditions may in different experiments greatly vary.†

With regard to the solubilities of tricalcic phosphate in carbonic acid water, and in solutions of chloride of ammonium, which I have already

* In the case of the tricalcic phosphate prepared for the last series of experiments, 11 litres of water were required to wash 13 grams of phosphate, the washing lasting many days.

† My own experiments show a much lower solubility of tricalcic phosphate in water than has been obtained by other chemists; probably their phosphates had not undergone a long previous washing by decantation. Voelcker, who gives the solubility as high as 1 in 12,589, possibly did not employ tricalcic phosphate, as his phosphate was prepared by pouring chloride of calcium into disodic phosphate, a plan which yields octocalcic triphosphate.

published, the results were all obtained before I was aware of the decomposing influence of water; as far as I am able to judge, however, tricalcic phosphate appears to have a definite solubility in these solutions, and is therefore probably dissolved in them unchanged.

Since it appears that all phosphates of calcium less basic than apatite are unstable under the continued action of pure water, it seems probable that a more exact examination of natural phosphates would show that many phosphates now regarded as tricalcic are in fact of a more basic nature.

XLI.—*On a New Tellurium Mineral.*

By J. B. Hannay.

While examining a very fine specimen of arsenical iron pyrites, I noticed on the lower side a small deposit of a metallic-looking substance, between which and the pyrites were a few scales of a substance like specular iron oxide, only they were rather of a brownish tinge, and wanted the brilliant black lustre of specular iron ore. A qualitative examination showed me that the metallic substance was tellurium, while the scaly substance consisted of tellurium, arsenic, and sulphur. The substance contained no water. The quantitative estimation of the elements was made in one portion, as I had very little substance to begin with. The following was the method employed:—

A weighed portion of the substance was dissolved in the smallest possible quantity of aqua regia, and a few drops of hydrochloric acid were added till the tellurous acid formed was all dissolved, but much heating was avoided to prevent loss of arsenic. The tellurium was then precipitated by stannous chloride and the metal collected on a weighed filter, then dried and weighed. To the filtrate from the tellurium, barium chloride was added, and the sulphur estimated as barium sulphate. In the filtrate the tin and arsenic were precipitated by hydrogen sulphide, and the precipitate collected on a filter and washed, then transferred to a beaker, and bromine-water added till all the arsenic was oxidized. The liquid was filtered to get rid of the stannic oxide, and to the filtrate containing the arsenic as arsenic acid, magnesian mixture was added, and the arsenic weighed as—

$$(NH_4)Mg'AsO_4 H_2O.$$

The substance was very easily oxidized by the acid; in fact it was attacked at once with brisk effervescence and evolution of red fumes, and on warming, all the tellurous acid formed soon dissolved. Continued heating was of course avoided, as this would occasion loss of

arsenic. The precipitate of metallic tellurium which comes down on the addition of stannous chloride is very easy to filter and wash, being flaky and slightly crystalline. The analyses yielded the following results:—0·6347 gram of the substance gave 0·2584 gram of metallic tellurium, 0·3978 gram of ammonio-magnesium arseniate, and 1·6453 gram of barium sulphate. The percentage composition as given below agrees almost exactly with the required amount for the formula $Te_2As_2S_7$, or $2TeS_2As_2S_3$.

	Found.	Calculated.
Tellurium	40·71	40·64
Arsenic	23·61	23·81
Sulphur	35·81	35·55
	100·13	100·00

The agreement of the analysis with the calculated amount is so close that it proves conclusively the constitution of the mineral. As my supply of the mineral was very small, and I did not know where to obtain any more, I determined to try to effect its formation by artificial means, in order that I might be able fully to examine its properties and molecular constitution, such as crystalline form, penetrability to light, and its conductive power for heat and electricity, as in a mineral of this class the investigation of these properties is of the utmost importance. The methods by which I attempted to form the mineral artificially have all given negative results. They were these:—1. Heating sulphide of arsenic with metallic tellurium. 2. Heating a mixture of the elements in the proportion to form the compound. 3. Heating sulphide of tellurium with sulphide of arsenic. In every case the arsenic sulphide volatilised alone, no arsenic remaining behind with the tellurium. These results showed that the elements which formed the mineral must have been under different circumstances when that formation occurred. The mineral was brought from a mine a considerable depth below the surface of the earth, showing that the elements while forming the compound must have been under great pressure. This, together with the heat acting for ages before the crust of the earth had cooled down, are the causes to which we must assign the formation of this curious compound.

XLII.—*On the Behaviour of Acetamide when heated with Sodium Alcohol.*

By W. N. Hartley, F.C.S., King's College, London.

With the view of obtaining methylamine, methylate of sodium was heated with acetamide, in the confident expectation that the following equation would be realised:—

$$\text{I.}\quad \left.\begin{matrix} C_2H_3O \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} CH_3 \\ Na \end{matrix}\right\}O = \left.\begin{matrix} CH_3 \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} C_2H_3O \\ Na \end{matrix}\right\}O.$$

It was within the bounds of possibility that the change might be represented by this next equation—

$$\text{II.}\quad \left.\begin{matrix} C_2H_3O \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} CH_3 \\ Na \end{matrix}\right\}O = \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} C_3H_5O \\ Na \end{matrix}\right\}O.$$

It is well known that Wanklyn considers that the hydrate of a radical called ethylene-sodium $(C_2H_4)''NaOH$ is formed when sodium is dissolved in alcohol and the product distilled to dryness.

Adapting this idea to the methyl-compound, the following result might be looked for—

$$\text{III.}\quad \left.\begin{matrix} C_2H_3O \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} CH_2Na \\ H \end{matrix}\right\}O = \left.\begin{matrix} H \\ H \\ H \end{matrix}\right\}N + \left.\begin{matrix} C_2H_3O \\ CH_2Na \end{matrix}\right\}O.$$

viz., ammonia and acetate of methylene-sodium. The last possibility is the formation of a compound of sodium-methylate and acetamide. Each of these possibilities has in turn at one time or another seemed, from incompleted experiments, to have been a reality, and some difficulty has been encountered in arriving at the truth, on account of the avidity for moisture of the materials used, and the falsity of the results caused by the presence of traces of water.

Extraordinary care was taken to prepare and keep the acetamide and sodium-alcohol perfectly dry and pure. At least six different trials were made, four with ethylate, one each with amylate and methylate of sodium. To prevent the action of atmospheric air on the products, the whole process was performed in a current of perfectly dry hydrogen. The scale on which the operations were conducted may be indicated by the following quantities: alcohol 1 litre, acetamide 60 grams, sodium 23 grams. Ammoniacal gas was in every case given off, and a crystalline substance left behind. This ammoniacal gas was found to be

ammonia, as the following figures show—ammonio-platinic chloride requires 44·18 per cent. of platinum.

		I	II	III
Weight of platinum salt..	=	1·0396	1·5738	1·4818 grams
Per cent. platinum......	=	42·9	44·6	43·93

		IV	V	VI	VII
Per cent. platinum......	=	43·92	44·1	43·69	43·63

Equation I is thus eliminated.

The residual white crystalline substance was proved not to be sodium propionate by its recrystallisation from absolute alcohol, solution in water, conversion into a silver salt and ignition.

0·7068 gram yielded 0·4554 gram Ag = 64 43 per cent. Sodium acetate would give 64·67, and sodium propionate 59·7 per cent. of silver. The substance is therefore sodium acetate. Actual combustion of the substance also led to the same conclusion. This disposes of Equation II.

The next experiments were made quantitatively—

Sodium.	Alcohol.	Acetamide.
10·7 grams	350 c.c.	27·4 grams

The distillate was fractionated at 100°—150° and 205°. The quantities of alcoholic ammonia given off, together with the actual ammonia, are here shown—

		Alcoholic ammonia. grams.	Actual ammonia.
Below 100°	....	40·6	0·8673
„ 150°	....	111·6	0·4704
„ 205°	....	60·0	0·1092
		Total ammonia evolved	1·4469

Acetamide should yield 28·81 per cent. of ammonia; this experiment gives only 1·4469 gram from 27·5 grams of acetamide, or only 5·2 per cent. of the obtainable amount. A second trial yielded a like result. The crystalline residue was converted by the action of water into acetate of sodium and ammonia. Equation III, therefore, does not hold good. When a solution of acetamide in slightly warm, absolute alcohol is added to a viscid cold solution of sodium-alcohol, the mixture slowly becomes a mass of beautiful large crystals, resembling cholesterin in appearance. From this mode of formation it might be concluded that a compound of sodium ethylate and acetamide is formed, and that this compound is not decomposed even at 200°. Certain fine specimens of this crystalline substance were examined with the micro-

scope, and found to be acetamide in the form of delicate, feather-like groups of crystals, encased by plates of sodium-ethylate. I have never succeeded in getting sodium-alcohol alone in such large crystals. It may be concluded, therefore, that no reaction takes place, and that no new compound is formed, but that, on admixture of acetamide, crystallisation is induced in a solution of sodium ethylate, which would otherwise remain in a viscid, fluid state. Even acetamide and sodium ethylate dried at 200°, when mixed and heated at various temperatures up to redness in a copper retort, do not yield a compound ammonia, an incondensable gas (probably marsh-gas) and ammonia being the products.

Besides showing the importance of making reactions quantitatively when possible, these experiments point out a very notable instance of departure from such a series of chemical changes as should be expected of a substance with the constitution usually accorded to sodium-alcohol.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

Crystallographical-optical Investigations with special reference to Isomorphous Substances. By H. TOPSÖE and C. CHRISTIANSEN (Copenhagen Scientific Society's Reports, 5th Series; Nat. Science and Mathematical Section, vol. 9).

THE investigations recorded in this paper were made for the purpose of supplying data for further testing the question as to whether there is any analogy between the optical and crystallographical characters of isomorphous bodies, Senarmont having made a series of researches with that object, but without finding any evidence of such analogy. His conclusion was that the causes determining the geometric form are of a distinct order from those which determine the doubly-refracting power, since this form remains the same in entire groups of isomorphous substances, whilst the optical properties experience in their essential elements, not only modifications in quantity, but a complete inversion of their relative magnitude.

The authors selected for the purpose of examination such isomorphous substances as would furnish the best series for comparison; and their object has been to make a complete investigation of the optical properties of each under all circumstances and relations. The list includes 11 regular forms, 36 having but one axis, 15 rhombic, and 18 monoclinic; amongst which are a number of double salts containing tin and platinum, as well as a long series of fluorides and selenates.

In the regularly crystalline bodies the determinations for the refractive indices of the lines C, D, and F, are given. In the case of the others the several indices for each line, the angle of polarization, the orientation, and the angles of the axes.

The refractive equivalents are calculated out according to the formula of Gladstone and Dale, as being the expression which appears to the authors most in accordance with the facts; and they come to the conclusion that the mean values of the refractive equivalents do not depend essentially on the crystalline form, but agree pretty nearly with the values deduced from the materials when in solution.

G. G.

Researches in Spectrum Analysis in connection with the Spectrum of the Sun. By J. NORMAN LOCKYER (Proc. Roy. Soc., xxi, 83 and 285—288).

THE author alludes to the advantages obtained by examining metallic spectra according to the plan which he has recently adopted, and shows that the origin of long and short lines in the spectrum is due to the

volatilisation of the metal in presence of atmospheric oxygen. Fourteen of the more commonly occurring metallic elements have been mapped on the new method.

It was observed as a fact that when the metallic vapour was submitted to a gradually decreasing pressure, the shortest lines disappeared first, and the longest lines remained longest visible. The study of the spectra of chemical compounds is commenced at this point, but it is more fully developed in the second communication. It is shown that the difference between the spectrum of a chloride and the spectrum of a metal is that, under the same spark conditions, all the short lines are obliterated, but that when the spark conditions vary, only the very longest lines in the spectrum are finally retained. The number of lines which remain appears to depend upon the atomic weight of the metal, since the greater the atomic weight, the smaller the number of lines which permanently remain.

The author has observed that the lines which are reversed in the solar spectrum are without exception the longest lines; upon this ground he adds zinc and aluminium to the list of solar elements, notwithstanding that Thalen had rejected zinc from Kirchhoff's list, and had agreed with him in rejecting aluminium.

Continuing the examination of the spectra of compounds and of mechanical mixtures, the spectra of the fluorides, bromides, chlorides, and iodides of lead, barium, strontium, magnesium, and sodium have been mapped. Of the lead compounds, the fluoride gave the greatest number of lines, and the iodide the smallest number, but in the sodium compounds the order was reversed, the iodide showing most of the metallic spectrum.

The difference between flame spectra and those produced by a weak electric discharge are discussed, and the results are compared with those of the low tension spark. It is shown that the difference is one of degree only; thus, barium bromide gives in the flame but one, and that the longest of the barium lines, whereas in the spark it gives 25 lines; in the former case the spectra of the metals in combination are invariably more simple than in the latter case, the shorter lines being always eliminated.

From the above experiments, the following conclusions are arrived at:—That a compound body possesses a perfectly definite spectrum. That the heat required to volatilise it and render its spectrum visible, decomposes the compound according to its volatility, and consequently that the number of true metallic lines which appear is to be considered as a measure of the decomposition.

Respecting mechanical mixtures, the spectra of several alloys containing different percentages of their constituent metals are given, and it is pointed out that the lines disappear from the spectrum as the percentage of any one constituent diminishes, the shortest lines always disappearing first.

The theoretical bearing of these results respecting solar and stellar spectroscopy is also discussed.

J. W.

The effect of Pressure on the Character of the Spectra of Gases. By C. H. STEARN and G. H. LEE (Proc. Roy. Soc., xxi, 282).

WHEN a current from an induction coil, with a Leyden jar interposed in the circuit, is passed through a tube containing a gas, say nitrogen, at atmospheric pressure, and the spectrum of the gas is examined, certain phenomena are observed. When the pressure of the gas is reduced, the appearance of the spectrum alters, becoming finally quite distinct from the original one; on the admission of fresh gas, the original spectrum reappears.

The authors show that these changes are *not* dependent on the density of the gas, but depend entirely on the intensity of the charge communicated to the Leyden jar.

The proof was obtained by passing the charge through two tubes, one of which was sealed, the other capable of being exhausted. On examining the spectrum of the sealed tube while the exhaustion of the other was proceeding, the same phenomena were observed as if the sealed tube itself had been in process of exhaustion.

When the pressure of the gas between the electrodes is high, the discharge does not take place until the jar is fully charged; but as the exhaustion proceeds, a less and less charge is communicated to the jar until the discharge becomes finally not greater than that of the simple current.

J. W.

Observations on a recent Communication of M. Chautard on the Absorption-bands of Chlorophyll. By A. MILLARDET (Compt. rend., lxxvi, 105—107).

THIS is a criticism of M. Chautard's communication (p. 341 of this volume), M. Millardet pointing out that the absorption-bands of a solution of chlorophyll were long ago examined and determined, and that it is unnecessary to examine such solutions spectroscopically in order to determine whether they have been recently prepared, or whether made from dried leaves, the colour of the solution being quite sufficient for that purpose. Moreover, as the identity of the chlorophyll in all vegetables has been proved, it is impossible to suppose that the nature of the plant, the climate, the temperature, the exposure or the soil, can exercise any influence on the composition of this pigment.

C. E. G.

Spectral Phenomena presented by different Solutions of Chlorophyll. By J. CHAUTARD (Compt. rend., lxxvi, 1066—1069).

CHLOROPHYLL is not absolutely insoluble in water, and the solution will stand ebullition, or keeping in the dark for weeks. If the water be acidified, the chlorophyll is absolutely insoluble. If it be alkaline, the characteristic black line is doubled. Alcohol, ether, and chloroform are excellent solvents of chlorophyll. The essential oils of basil, peppermint, hyssop, and lavender are equally good, provided

they are quite neutral, the slight acidity produced in them by age being quite enough to unfit them for this purpose. The mineral oils have the property of dissolving the green colouring matter with mere traces of the yellow. Consequently, such solutions exhibit the extreme bands of the blue and indigo without the necessity for a strong light. The solution of chlorophyll in carbon sulphide is of a deep olive colour, and when the layer of solution is thick enough it only allows the red and yellow rays to pass. With a thinner layer, if the sodium line of the spectrum be made to touch the 40th degree on the micrometer, four very distinct bands appear, one in the red, at 18°—25°, a second in the orange at 32°—35°, a third at the commencement of the green, at about 45°, and a fourth in the middle of the green at 55°, followed at 65° by a total extinction. If the stratum of solution be still thinner, a black band is seen in the red, a penumbra of the same size in the orange, the band between the yellow and the green has disappeared, a band extending from 65° to 75° separates the green from the blue, and from thence as far as 80°—85° the absorption of colour is complete. The last class of solvents of chlorophyll examined was that of fatty bodies, especially oils. These are divided into two sections, the first including oils completely destitute of action upon the prism (castor, almond, hazel-nut, nutmeg, and cocoa-nut oils), the second comprising those which themselves cause absorption of prismatic colours (colza, olive, linseed, and laurel-tree oils). The oils of beech-nut, hemp-seed, field-poppy, and palm-nut properly belong to the first class, although, with a very thick stratum, they have a slight power of absorption in the red region. This is due to traces of chlorophyll which they contain, derived from the fleshy envelope of the fruit, or from the cotyledons. The alcoholic extracts of all the above fruits and seeds have the same spectral characteristics as their oils. The alcoholic extract of (ripe ?) olives is peculiar in giving a double black band in the red, very similar to that produced by alkaline solutions of chlorophyll. The author thinks some explanation of this is to be found in the fact that the unripe olives gathered for eating are not considered to have arrived at perfection till they have been steeped in an alkaline solution. The chlorophyll obtained from dry leaves dissolves more easily than that from fresh leaves, owing to the absence of water in the first case. By this means it may be ascertained if an oil used in medicine, such as hemlock or belladonna, has been made from fresh or from dried plants. Those solutions of chlorophyll which contain no water resist the action of light for a very long period. This fact may explain the preservation of the chlorophyll of evergreens.

B. J. G.

Classification of the Absorption-bands of Chlorophyll; Accidental Lines. By J. CHAUTARD (Compt. rend., lxxvi, 1273—1275).

THE author divides the absorption-bands of the spectrum of chlorophyll into three classes :—1. The *specific* line in the red between B and C. 2. The *supernumerary* lines, including all the others which occur in

solutions of chlorophyll, whether recent or altered, neutral, acid, or alkaline; the most remarkable of these is that resulting from the splitting up of the specific line in the red under the influence of alkalis. Besides these, there is a third class of *accidental* lines, which are not permanent, and are only observed under special conditions. They are produced by the action of acids, and are formed by the splitting up of the red ray giving rise to other bands in the more refrangible portion of the spectrum near A, almost at the commencement of the red. The author gives a detailed account of the precautions necessary to be observed in order to insure success in this experiment, and also of the variations produced by the presence of other colouring matters, such as occur in red beetroot, red cabbage, and in St. John's wort.

C. E. G.

The Action of Light on the Electrical Resistance of Selenium. By Lieut. SALE, R.E. (Proc. Roy. Soc., xxi, 283—285).

THE electric conductivity of crystalline selenium has been observed to vary with the degree of light to which it is exposed. A bar of selenium was enclosed in a box and the resistance measured in the usual manner. On opening the box suddenly, and exposing the selenium to daylight, the resistance fell instantaneously and considerably; on exposing it in like manner to full sunlight, the resistance was so greatly diminished, that it was less by one-half than the measurement taken in darkness.

The bar was also exposed to the rays of the solar spectrum successively. The least resistance was observed in the extreme red rays, and the greatest in the violet and blue rays; it will be noticed, therefore, that the locus of the *maximum* heat rays is nearly coincident with the point of *minimum* resistance.

The spectrum of the electric light produced a very feeble effect, but the phenomena were identical with those produced by the solar spectrum.

The author has assured himself that the effect of varying resistances is not due to any change in the temperature of the bar of selenium.

J. W.

On the Heat of Transformation. By J. MOUTIER (Compt. rend., lxxvi, 365—368).

CERTAIN substances present themselves at the same temperature under two different conditions, which may be called M and M'. In passing from M to M', one kilogram of the body absorbs a quantity of heat, Q, *the heat of transformation.* Calling the heats of vaporisation L and L', the author has shown the following relation to hold—

$$(1.)\ Q = L - L'.$$

or in another form, as already given by Kirchhoff—

$$(2.)\ Q = \mathrm{AT}\, v\, p \frac{d}{dt} \log\left(\frac{p}{p'}\right)$$

where p and p' denote the vapour tensions of M and M', A = mechanical equivalent of heat, T = absolute temperature of the body, and V = the specific volume of the vapour of M.

Applications.—By means of the above equation we can calculate the quantity of heat absorbed on saturating one kilogram of water with sodium chloride. p and p' are in this case the tensions of water when pure and when saturated with common salt.

Regnault had found the difference in the tensions of a body in different states of aggregation to be extremely small: but he had left it undecided whether this difference was actually zero. The author deduces from the above equations that, for instance, ice and liquid water have slightly different tensions.

The minimum pressure, 0·6 atm., at 360°, at which, under the prolonged action of heat, the vapour of ordinary phosphorus deposits red phosphorus, may be considered as the maximum tension of red phosphorus at this temperature. The tension of ordinary phosphorus at this temperature is 3·2 atm., and as one litre of vapour of red phosphorus kept at 360° for 42 hours weighs 1·4 gram, so that $v = \frac{1 \text{ litre}}{1 \cdot 4}$ we can calculate the heat of transformation of ordinary into red phosphorus. It is $Q = - 17 \cdot 5$.

R. S.

On the Heat Disengaged in the Reactions between Water and the Hydrates of Potassium and Sodium. By M. Berthelot (Compt. rend., lxxvi, 1041—1048).

Potassium Hydrate.—One equivalent of perfectly anhydrous potassium hydrate yielded 12·46 heat-units on being dissolved in 100 parts of water. An equivalent quantity of the commercial potassium hydrate having the composition $KHO + \cdot 88H_2O$ yielded 4·6 heat-units. Under the same conditions, 12·46 − 4·6 h.-u. = 7·86 units; express, therefore, the heat evolved by the union of HKO with $\cdot 88H_2O$, from which we find 8·9 h.-u. as the quantity of heat evolved by the reaction (HKO,H_2O).

One equivalent of crystallised potassium hydrate of the composition $HKO + 2H_2O$, was found to absorb 0·03 h.-u. on being dissolved in water, so that the total heat evolved in the formation of $HKO + 2H_2O$ is 12·46 + 0·03 = 12·49 h.-u. If from this we subtract 8·9 h.-u., the heat-modulus of the reaction (HKO,H_2O), we obtain 4·12 h.-u. for the quantity of heat evolved in the formation of the second hydrate from the first.

The paper contains many determinations of the heat liberated on the addition of water to solutions of potash of different strength; by taking the quantities of water already combined with the potash as abscissæ, whilst the quantities of heat evolved on addition of water are represented as ordinates, the resulting curve was found to be a hyperbola of the equation $Q = \frac{23}{N_2}$ where n signifies the number of equivalents of water already combined with one equivalent of potassium hydrate. For values of $n < 11$ it is necessary to add the term

$-\frac{23}{10n}$ to which the right side of the equation is practically reduced when $n = 32$. The ordinates become negative for $n = 15$, or heat begins to be absorbed when water is added to HKO + 15 or more equivalents of water.

The following table exhibits the quantities of heat disengaged by the union of successive equivalents of water:—

$(KHO + 3H_2O) +$	H_2O	liberate	+ 0·90		
$(KHO + 4H_2O) +$	H_2O	,,	+ 0·42		
$(KHO + 5H_2O) +$	$2H_2O$	,,	+ 0·42	or + 0·21	for H_2O.
$(KHO + 7H_2O) +$	$4H_2O$	,,	+ 0·44	,, + 0·11	,,
$(KHO + 11H_2O) +$	$4H_2O$	,,	+ 0·20	,, + 0·05	,,
$(KHO + 15H_2O) +$	$17H_2O$	,,	+ 0·045	,, + 0·003	,,
$(KHO + 32H_2O) +$	$14H_2O$	,,	+ 0·015	,, + 0·001	,,
$(KHO + 46H_2O) +$	$9H_2O$	,,	+ 0·000		
$(KHO + 55H_2O) +$	$165H_2O$	,,	+ 0·026		

The quantities of heat disengaged decrease in a geometrical progression. A similar observation had been made by Hess in the case of sulphuric acid; but the attempt to express the numbers in both series as multiples of a common unit will most probably prove unsuccessful.

The molecular volumes of HKO + nH_2O do not seem to allow of a simple representation. The limit of contraction does not seem to be attained even when $n = 200$. The contractions take place in the same direction as the variations of the specific heats, which increase with the sum of the specific heats of water and potash.

Sodium Hydrate.—One equivalent of perfectly anhydrous sodium hydrate, on being brought together with 135 equivalents of water, disengaged 9·78 h.-u. One equivalent of the commercial sodium hydrate of the composition NaHO + $0·76H_2O$, disengaged 7·31 h.-u. From this we find 2·47 as the heat evolved in the combination of HNaO with $0·76H_2O$ and 3·25 as the number of heat-units liberated in the combination of one equivalent of HNaO with one equivalent of H_2O.

The quantities of heat evolved on adding water to solutions of soda of different concentration can be represented by an hyperbola of the equation $Q = \frac{23}{n_2}$, to the right side of which the term $- 0·6$ must be added for values of n between 5·6 and 18·4; for values of $n > 18·4$, it suffices to put $Q = -\frac{23}{2n}$.

The molecular volume of NaHO + nH_2O exhibits an increasing contraction which does not seem to have attained its limit when $n = 200$, and is much greater than that of equivalent potash-solutions. *The volume of dilute solutions of sodium hydrate is less than that of the water which they contain.*

In the case of potash-solutions, the molecular volume is greater than that of the water contained in them, although even here the molecular volume is less than the sum of the molecular volumes of the constituents—a fact which is general in the solutions of the fixed alkalis.

The difference of the molecular volumes of the solutions of potassium and sodium hydrates, is not exactly constant, but remains very nearly 9 c.c., a number not differing much from those which express the differences in the molecular volumes of the other salts of potassium and sodium.

R. S.

Condensation of a Mixture of Air and Steam upon Cold Surfaces. By OSBORNE REYNOLDS (Proc. Roy. Soc., xxi, 275—281).

WHEN pure steam is allowed to come into contact with a cold surface of sufficient extent to carry off the whole of its heat, the rate of condensation should be unlimited. If, however, the steam be mixed with a proportion of air, a little consideration will show that in all probability the rate of condensation would be greatly retarded. As a practical application of the latter assumption, it is proposed to send air into the boiler of a high-pressure engine, and to diminish in this manner the condensation at the surface of the cylinder, a plan which, if successful, would be much more elegant and efficient than that at present adopted.

The practical difficulties to be overcome in ascertaining the rapidity of condensation of pure steam were very great, and the measurement had to be conducted in an indirect manner. The steam was condensed in a vessel, in presence of hot water, and the extent of the vacuum attained in the interval between the condensation of the steam and the consequent ebullition of the water, was ascertained. The mercury of the gauge showed momentarily a perfect vacuum, and since the quality of the vacuum necessarily depended upon the rapidity of the condensation, the latter was shown to be practically instantaneous.

A very different and indeed, the anticipated result, was obtained when the steam was mixed with a small volume of air. On effecting the condensation, the mercury rose in the gauge to a short distance, and remained there.

The investigation being so far successful, the various effects of different quantities of air with the same volume of steam were compared. The results of experiment are minutely tabulated under three different heads, in each of which the conditions of the experiment were varied. In order to compare the results, the experimental numbers are reduced to uniformity by multiplying them by an arbitrary factor, and curves are plotted respectively, from the data so obtained.

The conclusions which may be legitimately drawn are as follows:—

1. That a small quantity of air in steam greatly retards its condensation upon a cold surface; that, in fact, there is no limit to the rate at which pure steam will condense but the power of the surface to carry off the heat.

2. That the rate of condensation diminishes rapidly and almost uniformly, as the pressure of air increases from 2 to 10 per cent. of that of the steam, and then less and less rapidly until 30 per cent. is reached, after which the rate of condensation remains nearly constant.

3. That by mixing air with steam before it is used, the condensation

at the surface of a cylinder may be greatly diminished, and consequently the efficiency of the engine increased.

4. That the maximum effect, or nearly so, will be obtained when the pressure of the air is one-tenth that of the steam, or when about 2 cubic feet of air at the pressure of the atmosphere, and temperature 15·5° C., are mixed with each pound of steam.

J. W.

A Miniature Steam-boiler Explosion. By Graeger (Chem. Centr., 1873, 97).

A solution from which a quantity of alcohol had been distilled in a glass flask, and containing about 5 per cent. sugar and as much gum, was allowed to cool again. On heating once more to boiling over a spirit lamp, the flask resting on wire gauze, the author noticed that the solution was an unusually long time before it began to boil, and just as he was about to remove the flask an explosion occurred, destroying some glass apparatus near at hand, but only damaging the flask to the extent of a small hole pierced in the neck. The accident was attributed to the fact that all air had been removed from the solution by the previous boiling, and that in heating up again the second time, the temperature of the solution had been raised considerably above the boiling point, when a position of unstable equilibrium was attained which the smallest shock was able to upset. It is recommended that solutions freed from air by previous ebullition be always shaken up well, to take up a little air, before boiling again.

W. S.

Inorganic Chemistry.

Direct Synthesis of Ammonia. By W. F. Donkin (Proc. Roy. Soc., xxi, 281).

The author, who has been conducting the researches of Sir Benjamin Brodie upon the action of induced electricity on mixtures of various gases, has succeeded in synthetizing ammonia by submitting a mixture of hydrogen and nitrogen in proper proportions to the same influence. The quantity of ammonia produced was small, but sufficient to give a very decided reddish-brown precipitate on the application of Nessler's test. No quantitative estimation was attempted.

J. W.

On the Reduction of Sulphuric Acid by Hydrogen. By G. J. Warner (Chem. News, xxviii, 13).

Pure hydrogen passed through sulphuric acid at 160°, or above, or heated in a sealed tube to 205°, with sulphuric acid or potassium bisulphate, causes the evolution of a large quantity of sulphurous anhydride. This did not take place with dried ferrous sulphate under similar conditions.

M. J. S.

Conversion of the Sulphates of the Alkalies into the Carbonates, Tartrates, &c., in the Moist Way. By J. LAWRENCE SMITH (Chem. News, xxvii, 316).

THE sulphates are dissolved in water saturated with carbonic acid. Pure barium carbonate is added, and the mixture shaken for some time in the cold; finally boiled and filtered. To prepare tartrates, oxalates, &c., from sulphates, heat the solution of the latter with excess of barium carbonate, and add gradually the requisite quantity of tartaric or other acid.

M. J. S.

Working of the Tellurium Vein of Nagyag in Transylvania. By A. SCHRÖTTER (Deut. Chem. Ges. Ber., vi, 552).

A NUMBER of foreign bodies, and in particular a great part of the antimony and arsenic, are removed by treating the ore, first with dilute, and then with concentrated hydrochloric acid, heat being applied in the latter case.

The ore is next washed as well as possible, and warmed with concentrated hydrochloric acid, and nitric acid diluted with its own volume of water is added so long as any reaction takes place. The mass is then well washed with water acidulated with hydrochloric acid, in order to obtain tellurium and antimony in solution. The filtrate is evaporated to drive off the nitric acid, and the gold precipitated by ferrous sulphate. After removal of the gold, the tellurium is obtained by precipitation with zinc or sulphurous acid. Or instead of this process, the gold and tellurium may be precipitated together from the first solution by sulphurous acid, and then separated from each other by nitric acid.

The residue left after the treatment with aqua regia, contains much quartz, silver chloride, lead chloride and sulphate, and antimony oxychloride. These metals can be extracted in various ways. One good method is to separate the finer from the coarser portions of the residue by a fine sieve, and then to reduce the metallic salts contained therein by zinc. The mass is dried after complete reduction has taken place, and heated, with addition of lead, till the zinc is expelled as chloride.

The silver is extracted from the residue by boiling with concentrated sulphuric acid.

G. T. A.

On Some Compounds of Glucinum. By A. ATTERBERG (Bull. Soc. Chim. [2], xix, 497).

The hydrate is precipitated as a white gelatinous mass by ammonia from a solution of glucinum chloride. Dried at 100° it has the formula GlO_2H_2. When a solution of glucina in potash is boiled, the hydrate precipitates as a compact powder, free from alkali, and having the composition $3GlO_2H_2.H_2O$.

Sulphate, $GlSO_4 + 4H_2O$. This salt loses two molecules of water

at 100°, the third at 150°, and the fourth at a higher temperature. Under a prolonged red heat, all its acid is expelled. It does not form a double sulphate with ferrous or cupric sulphates.

Basic sulphate.—*a.* $GlSO_4.GlO_2H_2 + 2H_2O$.—Formed by dissolving glucinum hydrate or carbonate in a solution of the neutral sulphate. It is a transparent, amorphous mass, which, when dried at 100°, has the above composition. At 200° it loses two molecules of water.

b. $GlSO_4.5GlO_2H_2 + 2H_2O$ is produced when the solution in which it is formed is boiled.

Potassio-glucinic Sulphates.—*a.* $\left.\begin{matrix}K_2\\Gl\end{matrix}\right\}(SO_4)_2 + 2H_2O$. A white crystalline powder, little soluble in cold water, but easily soluble in warm water.

b. $\left.\begin{matrix}K_2\\Gl\end{matrix}\right\}(SO_4)_2 + 2KHSO_4 + 4H_2O$ is precipitated by the addition of sulphuric acid to a mixed solution of the two sulphates. At 100° it loses $4H_2O$.

Sodio-glucinic sulphate, $3GlSO_4.2Na_2SO_4 + 12H_2O$, forms needles, grouped in stars, unalterable in the air, and giving off $7H_2O$ at 100°.

Ammonio-glucinic Sulphate, $GlSO_4,(NH_4)_2SO_4 + 2H_2O$, gives off 2 mol. water at 110°.

Selenate, $GlSeO_4 + 4H_2O$.—A very soluble salt which loses $2H_2O$ at 100°.

Selenite.—A solution of glucina in selenious acid does not furnish crystals by evaporation; but ammonia gives a white flaky precipitate of $2GlSeO_3.GlO_2H_2 + 5H_2O$, which loses $3H_2O$ at 100°.

Sulphite.—When a solution of glucina in saturated aqueous sulphurous acid is evaporated, part of the acid escapes, and a viscous basic salt is obtained, probably having the composition $GlSO_3.GlO_2H_2 + 2H_2O$.

Hyposulphite.—Cannot be crystallised; its solution when evaporated evolves sulphurous acid.

Chromate.—A solution of glucinum oxide in chromic acid does not furnish crystals by evaporation. The addition of neutral potassium chromate to a solution of glucinum sulphate precipitates a basic salt, which is decomposed by washing with water.

Molybdate, $GlMoO_4.GlO_2H_2 + 2H_2O$.—Obtained in fine needles, almost insoluble, by prolonged ebullition of glucinum hydrate with molybdic acid.

Double Chloride of Glucinum and Mercury, $3HgCl_2.2GlCl_2 + 6H_2O$.—Crystallises in large well-developed tables, and is very hygroscopic.

The solution of *glucinum chlorate* decomposes by concentration. The *iodate* remains, after evaporation, as a gummy mass.

J. B.

On the Atomic Weights of Cerium, Lanthanum and Didymium. By D. Mendelejeff (Deut. Chem. Ges. Ber., vi, 558—560).

In this paper the author confirms the new atomic weights which he had previously assigned to these metals (*Ann. Ch. Pharm.*, Supp. viii, 133), and ascribes the formula $Ce_2O_3(SO_3)_3.Ce_2O_4(SO_3)_4 + 24H_2O$

(Ce = 138) to the reddish brown cerium salt of Rammelsberg, $3CeSO_4.Ce_2(SO_4)_3+21H_2O$ (Ce = 92). To Rammelsberg's second salt, $CeSO_4.2[Ce_2(SO_4)_3].9[(NH_4)_2SO_4]+12H_2O$ (Ce = 92), he assigns the formula $Ce(SO_4)_2.3[(NH_4)_2SO_4]+4H_2O$ (Ce = 138), which agrees better with the results of Rammelsberg's own analyses.

The author divides all the cerium salts into three classes, cerous salts (Ce_2X_6 or CeX_3); cerosoceric salts ($Ce_2X_6Ce_2X_8$ or Ce_2X_7, formerly Ce_3X_8), and ceric salts (Ce_2X_8 or CeX_4, formerly Ce_3X_4). In reply to Rammelsberg's objection that ceric oxide (CeO_2 according to Mendelejeff) decomposes hydrochloric acid, whereas the dioxides TiO_2 and ZrO_2 of the same group do not, the author says that the same reasoning would prove H_2SO_4 and H_2TeO_4 not to be analagous, and it is quite possible that in the series TiO_2, ZrO_2, CeO_2, LaO_2, ThO_2, ceric oxide may possess the characters of a peroxide, being intermediate in properties between the two acid and the two basic dioxides.

Similarly the objection that didymium oxide is isomorphous with cadmium oxide, and cerium oxide with magnetic iron ore, would apply equally to the case of the isomorphism of $FeNb_2O_6$ and $FeWO_4$, and to that of Ta_2O_5, WO_3 and TiO_2.

C. E. G.

On the Behaviour of Alum towards the Chromates of Potassium and Barium, and the Reasons why a Chromic Acid Alum cannot be formed. By E. Fleischer (Arch. Pharm. [3], ii, 300—304).

The author endeavoured to produce a chromic acid alum, first by the action of barium chromate upon alum; secondly, by means of calcium chromate; thirdly, by direct combination of aluminium chromate with potassium monochromate.

All attempts failed: in the last case, because potassium monochromate decomposes neutral aluminium chromate, forming potassium bichromate and basic aluminium chromate; and in the first two cases, because the action is very slow, and alumina is precipitated as chromate.

A further reason why such an alum cannot be formed, is that chromic acid, like vanadic, tungstic, molybdic, and titanic acids, forms, for the most part, anhydrous salts with which it will readily combine, giving rise not only to double, but also to multiple acid anhydrous salts.

G. T. A.

Action of Nitric Acid on Lead Chromate. By E. Duvillier (Compt. rend., lxxvi, 1353).

After boiling lead chromate for ten minutes with twice its weight of concentrated nitric acid, it is almost entirely decomposed into chromic acid and lead nitrate, which is insoluble in the nitric acid. The solution contains only 2 molecules of PbO to 100 of CrO_3. On addition of water, the lead chromate is again precipitated.

B. J. G.

On the Action of Water on Lead.

By Sir ROBERT CHRISTISON, Bart. (Chem. News, xxviii, 15).

THE purest waters act most powerfully on lead. All salts impede this action, and nearly in the inverse ratio of the solubility of the compounds which their acid forms with lead oxide.

Some salts, when in comparatively strong solution, assist the action which in weaker solution they impede. Disodic carbonate renders even a hard water capable of attacking lead; the monosodic salt does not. Lead cisterns should be soldered autogenously, and carefully protected from galvanic action.

M. J. S.

On the Reduction of Pure Anhydrous Ferric Oxide with Pure Carbon in Vacuo.

By JOHN PARRY (Chem. News, xxvii, 313).

FERRIC oxide was prepared by reducing ferrous oxalate in pure hydrogen, dissolving the iron in hydrochloric acid, oxidising, precipitating with ammonia, washing, drying, and igniting. It contained merely a trace of sulphur. Carbon was obtained by heating white sugar gradually to the fusing heat of iron in a vacuum (produced by Sprengel pump).

From a mixture of these substances, heated *in vacuo*, no gas was evolved at 100°, but at temperatures rising from the melting point of lead to that of copper, 77 per cent. of the oxygen in the ferric oxide was removed in seventeen hours, slowly at the lower temperatures, the gas consisting principally of carbon dioxide, and rapidly at higher temperatures when carbon monoxide was chiefly evolved.

The author concludes that the reducing action of solid carbon may play some part in the chemistry of the blast furnace.

M. J. S.

The Solubility of Arsenious Acid in Water.

By L. A. BUCHNER (N. Repert. Pharm., xxii, 265—273).

FRESH determinations of the solubility of the vitreous and crystalline varieties of arsenious acid in water which, as a whole, confirm the results arrived at by Bussy.

The crystalline modification, when shaken with cold water and allowed to stand for 24 hours, dissolves in 355 parts, while the amorphous variety dissolves in 108 parts only under the same circumstances. One part of the crystallised acid is dissolved in 46 parts of water when the solution is made at the boiling temperature, and then allowed to stand for 24 hours at 15° C. The amorphous acid treated as in the last case, remains dissolved in about 30 parts of water.

C. H. G.

Formation of Crystalline Antimony.

(Dingl. polyt. Jour., ccvii, 427).

The antimony is deposited on copper from a hydrochloric acid solution of antimonious chloride. On removing it, and pulverising it in a mortar, it detonates, and is changed from the amorphous to the crystalline condition. The author has not observed if this result is produced by heat, as is the case with rhodium and iridium.

W. R.

The Precipitation of Silver by Copper. By Alfred Tribe

(Brit. Assoc. Report, 1872. Trans. of Sections, 84).

Mineralogical Chemistry.

On the Crystalline System of Leucite. By G. vom Rath

(Jahrbuch f. Mineralogie, 1873, 113—124).

The crystals of leucite implanted in the druses of certain outcasts from Vesuvius (p. 146 of this volume), are characterised by a peculiar striation, the lines running parallel either to the shorter (so-called hexahedral) edges, or to the symmetric diagonals of the trapezoïdal faces. These lines often begin in the middle of a face and are not continued to an edge; but when one of them reaches an edge, it does not usually stop there, but is prolonged into the adjoining face, the line and its prolongation being situated in a plane, which, assuming the form of leucite to be the regular icositetrahedron, is parallel to the truncation-face of the symmetrical summits of the crystal, or in other words, to the face of a rhombic dodecahedron. Moreover, the striæ have a very perceptible breadth, and their surface shines in a position different from that in which the general face of the crystal on which they occur appears lustrous, the bands remaining dark while the general surface is bright, and *vice versâ*. In short, the striation of these implanted leucites exhibits the closest possible analogy to that of triclinic felspar, which is known to arise from the interposition of twin-lamellæ.

From the appearances above described, it may be inferred with certainty that these striated leucites do not belong to the regular or monometric system: for in that system a twin-formation parallel to a dodecahedral face cannot occur. If indeed an icositetrahedron be cut parallel to the face of the dodecahedron and turned round 180°, no projecting or re-entering angles will be formed, but the whole will return into its former position.

The conclusion thus deduced is confirmed by exact measurements of the angles of the leucite crystals, from which it appears that edges which ought to be identical if the crystals were monometric, really differ by about 4 degrees.

Leucite belongs in fact to the quadratic or dimetric system, its form, hitherto regarded as a regular icositetrahedron, or leucitohedron, being a combination of a quadratic octohedron with a dioctohedron:

Octohedron.....	a,	a,	c,	or P
Dioctohedron....	$\frac{1}{4}a$,	$\frac{1}{2}a$,	c,	or 4P.2.

These faces exhibit a remarkable equality of development. The following also sometimes occur subordinate:

First acute octohedron......	$\frac{1}{2}a$,	∞a,	c	or 2P∞
First quadratic prism	a,	a,	∞c,	or ∞P.

The ratio of the lateral axes to the vertical axes, deduced from the measurement of the lateral edge of the dioctohedron, is—

$$a : c = 1\,8988 : 1, \text{ or } 1 : 0{\cdot}05637.$$

The following are the principal angles:—

Terminal edge of the octohedron	= 130° 3′
Lateral	= 73° 19′ 40″
Primary terminal edge of the dioctohedron (situated under the octohedral edge) ..	= 131° 23′
Secondary lateral edge (situated under the octohedral face)	= 146° 9′ 30″
Basal angle of the dioctohedron (situated at the ends of the lateral axes)	= 126° 52′ 15″
Basal angle of the dioctohedron (situated between the lateral axes)..............	= 143° 7′ 45″.

The plane angles of this base are the same as those of the three sections through the octohedral edges of the icositetrahedron 2O2.

The law of twin-formation of leucite is that "The twin-plane is a face of the first acute octohedron;" and by this plane the crystals are united. The twin-plane is inclined to the vertical axes at an angle of 43° 31′; to one of the lateral axes at 46° 28′ 15″. Leucite, hitherto supposed to be incapable of forming twins, is in reality very much inclined to twin-formation, exhibiting very regular combinations of two or more individual crystals, and also polysynthetic crystals in which, as above described, the principal crystal is intersected by laminæ parallel to the faces of the first acute octohedron.*

Imbedded leucites do not admit of exact angular measurement, but they frequently have obtuse projecting and re-entering angles, and exhibit the polysynthetic structure in a very high degree. There can, therefore, be little doubt that they are also quadratic, like the implanted crystals.

The chemical analysis of leucite crystals from the same druse as those whose angular measurement has been above given, exhibits the following composition—

SiO_2.	Al_2O_3.	CaO.	K_2O.	Na_2O.	
55·21	23·70	0·43	19·83	1·21	= 100·38

agreeing almost exactly with the leucite formula, $K_2O.Al_2O_3.4SiO_2$, which requires 54·92 SiO_2, 23·52 Al_2O_3, and 21·56 K_2O. The proportion of soda in these striated crystals is not greater than in crystals of leucite previously examined, and regarded as monometric (Rammels-

* The original paper contains full descriptions, illustrated by diagrams, of several of these twin-formations.

berg found 6·40 p.c. Na_2O in a Vesuvian leucite): consequently the quadratic form cannot be regarded as a peculiarity of these crystals due to the presence of soda.

The optical characters of leucite are more in accordance with the quadratic than with the hitherto assumed monometric form. Des Cloizeaux (*Nouvelles recherches sur les propriétés optiques des cristaux*, 1867, pp. 3—5), observes that leucite, when examined by polarised light, does not behave like a monometric crystal, the appearances varying according to the particular plate examined, and the direction in which it has been cut from the crystal. He also remarks that the striæ seen in polarised light are parallel to the planes of a dodecahedron. These striæ, due to interposed twin-lamellæ, had been previously observed by Biot, who founded upon them his theory of lamellar polarisation.

Leucite may now take its place amongst the series of quadratic minerals which are so characteristic of Vesuvius, viz., zircon, humboldtilite, meyonite, mizzonite, sarcolite and vesuvian, to the last of which it approximates very closely. The primary form of vesuvian has, according to v. Zepharovich, an angle of 129° 20′ in its lateral edges, and amongst its numerous combinations there occurs the dioctohedron 4P2, which is otherwise not frequently observed. If the primary form of vesuvian were further associated with the dioctohedron 4P2, a form would be produced almost exactly like the regular icositetrahedron, as in the case of leucite.

H. W.

Mica Spherules from Hermannschlag in Moravia.

By G. Tschermak (Jahrbuch f. Mineralogie, 1873, 191).

These spherules are from 2·5 to 7·5 centimeters in their longer diameter, and always appear somewhat flattened. The outermost crust consists of laminæ of biotite, placed normally to the radius of the nodule. The biotite has an optical axial angle of about 12°, and a dark-brown colour, approaching nearly to brass-yellow in the weathered state. Below the biotite is a concentric layer, at most a centimeter thick, of a greenish-white fibrous mineral, the fibres of which run parallel to the radius of the nodule. This mineral is anthophyllite, cleaving in the direction of a prism of 55°, also in that of the transverse surface. Qualitative analysis shows that it contains chiefly silica and magnesia, together with iron and a little alumina. Below this layer of anthophyllite is the nucleus, also consisting of laminæ of biotite, which, in the outmost layer, are nearly perpendicular to the radii of the nucleus. This biotite is exactly like that of the crust, has a dark-brown colour in the fresh state, but the angle of its axes is smaller than that of the external biotite, viz., 5°. It should, therefore, also differ somewhat in composition from the outer layer.

Between the layer of anthophyllite and the biotite nucleus there is sometimes interposed a sea-green layer, which exhibits the characters of a mixture of talc and chlorite; and since the remains of cleavage point to diallogite, this layer is probably a decomposition-product of such a mineral.

The complete development of these nodules exhibits, therefore, three concentric layers, and a nucleus, namely from the centre outwards; biotite, anthophyllite, talc, biotite. There is no doubt that these several minerals have been produced by transformation of a single original mineral, but the nature of that mineral cannot at present be determined.

H. W.

Arseniferous Uranium Mica (Zeunerite) from Joachimsthal. By G. Laube (Jahrbuch f. Mineralogie, 1873, 191).

The expectation of Auerbach (*Jahrbuch*, 1872, 206) that zeunerite would be discovered amongst copper-uranium mica (chalkolite) has been verified by Laube on a specimen from the Geisterholde, near Joachimsthal. He obtained emerald-green crystals of uranium mica of remarkable beauty, having the form 0P . P . ∞ P, with basal cleavage. An analysis by Gintl showed them to contain uranic oxide, cupric oxide, arsenic acid, and water, and indeed to have the composition of zeunerite, as determined by Weisbach (p. 150 of this volume), and by Winkler (*ibid.*, 607).

H. W.

On Serpentine. By R. Drasche (Deut. Chem. Ges. Ber., vi, 555).

Serpentine microscopically considered can be divided into two classes, the first of which contains olivine, some magnetic oxide of iron, and bronzite or diallage. Rocks of this kind have approximately the theoretical formula of serpentine. They are found at Kraubat in Styria, Snarum in Norway, Easton in Pennsylvania, &c.

Rocks of the second class, seen under the microscope, consist of a rhombic mineral which has a ready cleavage, some magnetic oxide of iron, and diallage or bronzite.

In chemical composition they agree partly with serpentine, and in part differ considerably. Thus a serpentine from Heiligenblut contains only 8·4 per cent. of water. In respect of hardness, they consist of two minerals at least, one of the hardness of talc, another of that of felspar. The author considers, from the analyses compared with those of bronzite and bastite, that rocks of the second class are bronzite-bastite-rocks, and that their varying chemical composition is due to excess or deficiency of one or other of the constituents. Rocks of this kind occur at Heiligenblut in Carinthia, Mayo in Ireland, &c.

G. T. A.

On the Constitution of Atacamite. By H. Ludwig (Deut. Chem. Ges. Ber., vi, 553).

When atacamite is carefully heated, aqueous vapour is driven off and a mixture remains of copper oxide and chloride, the latter of which can be extracted by water. The decomposition begins at 220°, but even at 250° is so slow that it requires several days for its completion. If

the temperature exceeds 250°, hydrochloric acid is given off as well as aqueous vapour, owing to the action of the water on the copper chloride.

If atacamite is heated with water in a closed glass tube to 200° for several hours, no change takes place.

Hence this mineral can no longer be regarded as a molecular compound of copper oxychloride with water, or of copper chloride with hydrated copper oxide. We must suppose that it contains a nucleus of copper atoms combined with chlorine and hydroxyl groups, and must, therefore, consider copper a quadrivalent element.

The empirical formula of atacamite being—

$$Cu_2ClO_3H_3, \text{ or doubled, } Cu_4Cl_2O_6H_6,$$

the rational formula will be expressed thus:—

$$\begin{array}{l} Cu(OH)Cl \\ \| \\ Cu(OH)_2 \end{array} \quad \text{or} \quad \begin{array}{ccc} Cl_2Cu & — & Cu(OH)_2 \\ | & & | \\ (OH)_2Cu & — & Cu(OH)_2. \end{array}$$

Similarly brochantite ($Cu_4SO_{10}H_6$) may be written thus—

$$\begin{array}{ccc} (SO_4)Cu & — & Cu(OH)_2 \\ | & & | \\ (OH)_2Cu & — & Cu(OH)_2 \end{array} \quad \text{or} \quad \begin{array}{ccccccc} (OH)_2Cu & = & Cu & —(SO_4)— & Cu & = & Cu(OH)_2. \\ & & | & & | & & \\ & & (OH) & & (OH) & & \end{array}$$

The constitution of other copper compounds, such as malachite, chessylite, and the artificial basic salts, may be explained much better in this way than by the supposition of molecular grouping.

G. T. A.

Composition of Ashes from Vesuvius. By C. OSTERLAND and P. WAGNER (Deut. Chem. Ges. Ber., vi, 285).

SACCHI suggested that volcanic ashes are produced and carried into the air by strong currents of vapour acting upon the solid particles imbedded in the lava (leucite in that of Vesuvius). Rammelsberg has shown by analysis that the ashes are simply finely-powdered lava. The authors examined some ashes collected at Naples during a calm in 1872; and came to the same conclusion as Rammelsberg, except that they found 1·41 per cent. of alkalis and ·9 per cent. of phosphoric acid, while Rammelsberg's analyses give 9 63 per cent. of alkalis and no phosphoric acid.

G. T. A.

Crystallography—Sphene from the Eisbrückalp, Tyrol. By F. HESSENBERG (Jahrbuch f. Mineralogie, 1873, 182).

Beryl. By A. SCHRAUF (*ibid.*, 183).

The Crystalline Forms of Pucherite from Schneeberg. By M. WEBSKY (*ibid.*, 183).

On Cœlestin from Rudersdorf and Mokattam. By Arzruni (Jahrbuch f. Mineralogie, 1873, 184).

Axinite from Botallack, in Cornwall. By F. Hessenberg (*ibid.*, 186).

Hemimorphism in Calcspar. By Max Bauer (*ibid.*, 190).

Tridymite imbedded in Rock-crystal. By K. Vrba (*ibid.*, 190).

Analysis of the Mineral Water of Mattigbad (Mattighofen, Upper Austria). By Th. Laugeb (Arch. Pharm. [3], ii, 304—306).

The chief salts in this water are sodium bicarbonate (·0684 per cent.), calcium sulphate (·0247 per cent.), sodium chloride (·0186 per cent.). Besides these it contains in smaller quantities the carbonates of iron, calcium, and magnesium, calcium phosphate, etc., and free carbonic acid.

G. T. A.

General Results of the Analysis of the Geysers on the Island of San Miguel (Azores). By Th. de Fouqué (Compt. rend., lxxvi, 1361—1364).

The valley of Furnas in the eastern part of San Miguel was disturbed about three centuries ago by volcanic eruptions, and the soil is now perforated by a number of geysers. The three largest and most active of these have received the name "caldeiras." One of these only furnishes a continuous stream of water. Another sends forth intermittent currents; while the third emits only water-vapour and gas. Besides these boiling springs, there exist others which possess a temperature of about 16° C. (?), and whose waters are ferruginous. The water of some is very alkaline and but slightly sulphurous; others are not in the least sulphurous; many contain a considerable amount of hydroferric carbonate and carbonic acid; and some, free sulphuric acid. These springs, especially those containing sulphuric acid, are used medicinally. All of them contain a large quantity of silica in solution, so large, indeed, that it is deposited at the mouth. Soda salts and free carbonic acid are present in large quantity, while iron, lime, and magnesia are comparatively scarce. Several of the springs contain traces of bromides, iodides, and fluorides; boracic acid and arsenic are not present.

W. R.

Organic Chemistry.

Formation of Carbon Tetrabromide. By J. Habermann (Deut. Chem. Ges. Ber., vi, 549).

When bromoform containing bromine is covered with a layer of dilute alkali and left to itself, it often becomes converted after a time into carbon tetrabromide, and this change appears to be due to the influence of light. By exposing mixtures of this kind to direct sunlight and diffused daylight, and comparing them with others kept in the dark, it was found that, in the first case 20 grams of bromoform required 5—6 days, in the second twice the time, while in the dark scarcely a trace of CBr_4 was formed.

Water alone may be used, but the process then requires a much longer time.

G. T. A.

The Mineral Oils of Buxière-la-Grue and Cordesse. By J. Joifre (Bull. Soc. Chim. [2], xix, 547—550).

The mineral oils extracted from bituminous schists for commercial purposes do not differ in physical properties from American petroleum, but, as the author finds, they behave differently when treated with certain chemical reagents. American petroleum, consisting of saturated hydrocarbons, is unattacked by fuming sulphuric acid and monohydrated nitric acid. When, however, the mineral oils are treated with fuming sulphuric acid, a partial absorption takes place; when with nitric acid, nitrated products are formed. The part unattacked is not acted upon by a mixture of the two acids, and undergoes oxidation by nitric acid only at boiling-point. The boiling-points and densities of different portions—separated by fractional distillation—agree with those of the saturated hydrocarbons (C_nH_{2n+2}), and elementary analysis also shows that they belong to this series. These hydrocarbons form 50 p. c. of the oil, and are regarded by the author as identical with those extracted by Pelouze and Cahours from American petroleum. By fractional distillation he obtains a series of saturated hydrocarbons from octane (C_8H_{18}) up to heptadecane ($C_{17}H_{36}$).

The part attacked by sulphuric acid consists apparently of hydrocarbons of the ethylene series (C_nH_{2n}) together with less hydrogenised hydrocarbons. They are violently attacked by bromine. They do not contain benzene or naphthalene, probably because these commercial mineral oils are distilled at the lowest possible temperatures.

C. C.

Amylenes. By F. Flavitzky (Deut. Chem. Ges. Ber., vi., 562).

This is a preliminary notice on two amylenes, one of which, obtained by the action of alcoholic potash on the amyl iodide from inactive fermentation alcohol, boils at 25°, and combines with bromine at the

ordinary temperature. This amylene, when heated in closed tubes to 100° with strong hydrochloric acid, combines with it, and forms a hydrochloride, which boils at 85° to 86°, and is decomposed when boiled with water, yielding an alcohol. The other amylene, obtained by the action of phosphoric anhydride on ethyl-amyl ether, boils at 35°. A gas is evolved during the reaction, probably ethylene.

C. E. G.

On Ethyl-acetylene and its Identity with Crotonylene.

By L. PRUNIER (Compt. rend., lxxvi, 1410—1413).

ETHYL-ACETYLENE was produced synthetically by Berthelot by passing a mixture of acetylene and ethylene through a tube heated to low redness.

The author has repeated this experiment, and from the resulting hydrocarbon has prepared the tetrabromide, $C_4H_6Br_4$, by contact with excess of bromine. This bromide agrees in composition and properties with the crotonylene tetrabromide described by Caventou.

The constitution of crotonylene is thus established. It is, in fact, ethyl-acetylene.

W. A. T.

Preparation of Methyl Iodide and Butyl Iodides.

By A. BUTLEROW (Deut. Chem. Ges. Ber., vi, 561—562).

METHYL alcohol and the requisite quantity of red phosphorus are heated in a flask furnished with two condensing tubes, the iodine being gradually added through the wider of the two tubes. In this apparatus a kilogram of the iodine can be converted into the iodide in five or six hours.

In order to prepare *isobutyl iodide*, the author passes washed hydriodic acid into boiling isobutylic alcohol. The hydriodic acid was prepared by allowing water to flow slowly into a vessel containing phosphorus iodide, prepared by the direct addition of ordinary phosphorus to iodine. 500 grams of the alcohol yielded 1250 of the iodide.

Tertiary butyl iodide is prepared by passing isobutylene into an aqueous solution of hydriodic acid saturated at 10°. The isobutylene from 200 grams of isobutyl iodide yielded 130 to 140 grams of tertiary butyl iodide.

C. E. G.

On the Boiling-points and Molecular Volumes of the Isomeric Chloro-derivatives of the Ethylic Series.

By G. HINRICHS (Compt. rend., lxxvi, 1408—1410).

THIS is a discussion of the properties of the isomeric chlorinated derivatives of ethylene and hydride of ethylene in relation to the author's theory of molecular mechanics.

W. A. T.

On the Combinations of Titanium Chloride with Ethers.

By E. DEMARÇAY (Compt. rend., lxxvi, 1414—1417).

TITANIUM chloride is capable of combining with oxygenated ethers as well as with the sulphides and sulphydrates of alcohol-radicals. The compounds thus formed with the ethers of monobasic acids belong to three types, which may be represented by the following formulæ, in which E and E′ stand for a molecule of the ether:—

$$[TiCl_4]_2E, \quad TiCl_4E, \quad TiCl_4EE'.$$

The ethers of dibasic acids furnish corresponding compounds—

$$[TiCl_4]_4E, \quad [TiCl_4]_2E, \quad TiCl_4E.$$

These compounds are all formed by mixing together chloride of titanium and the ethers in proportions corresponding with the formulæ. They are all solid, yellowish, non-volatile bodies, which are decomposed by heat, and are obtained in distinct crystals only with difficulty.

The author considers that these compounds are most probably double chlorides containing a chlorhydrin united to the chloride of an acid radical. The compounds formed with ethyl acetate, for example, have the following composition:—

$$2[TiCl_4].C_2H_3O_2C_2H_5.$$
$$TiCl_4.C_2H_3O_2C_2H_5.$$
$$TiCl_4.2[C_2H_3O_2C_2H_5].$$

These formulæ may be otherwise written—

$$TiCl_3(OC_2H_5).TiCl_4\,C_2H_3OCl.$$
$$TiCl_3(OC_2H_5).C_2H_3OCl.$$
$$TiCl_2(OC_2H_5)_2.2(C_2H_3OCl).$$

The sulphides and sulphydrates of alcohol-radicals behave with chloride of titanium in the same manner as the oxygenated ethers.

W. A. T.

On various Propylene Chlorides.

By E. REBOUL (Compt. rend., lxxvi, 1270—1272).

OF the four possible propylene chlorides, namely:—

1. $CH_2Cl—CH_2—CH_2Cl.$ Normal chloride of propylene.
2. $CH_3—CHCl—CH_2Cl.$ Ordinary chloride of propylene.
3. $CH_3—CCl_2—CH_3.$ Methylchloracetol, or dichlorhydrate of allylene.
4. $CH_3—CH_2—CHCl_2.$ Chloropropylol.

the first and third are known, and the author has now prepared and described the other two.

I. *Normal Chloride of Propylene*, $CH_2Cl—CH_2—CH_2Cl$.—The author at first endeavoured to prepare this, the true homologue of

ethylene dichloride, by the action of hydrochloric acid on chloride of allyl, but found that he obtained only the ordinary chloride of propylene. The action of hydrobromic acid on bromide of allyl, however, yields very different results. Ordinary bromide of propylene boiling at 143° is indeed formed, but also the normal bromide boiling at 162° to 163°, the best conditions for the formation of the latter being to heat the allyl bromide with the most concentrated hydrobromic acid to 100° in closed tubes for twelve minutes. The normal bromide, $CH_2Br—CH_2—CH_2Br$, is easily transformed into the chloride by means of dichloride of mercury. It is a liquid boiling at 117°, and closely resembling ethylene dichloride in its properties. Its density at 15° is 1·201. Alcoholic potash converts it first into allyl chloride, $CH_2—CH—CH_2Cl$, and ultimately into ethyl-allylic ether, $CH_2—CH—CH_2(OC_2H_5)$.

II. The author has also afforded additional proof that the methylchloracetol prepared by the direct union of hydrochloric acid and allylene is identical with that obtained by the action of phosphorus pentachloride on acetone, inasmuch as both of them yield the same crystals of benzoate, $CH_3—C(C_7H_5O)_2—CH_3$, when treated with silver benzoate.

III. *Chloropropylol*, $CH_3—CH_2—CHCl_2$.—When pure normal propylic aldehyde is added drop by drop to a slight excess of phosphorus pentachloride, a brisk reaction takes place, and the product yields a new compound on distillation, mixed, however, with phosphoric oxychloride. After removal of the latter by washing with water and treatment with potash, a liquid is obtained which boils between 84° and 87°. This is chloropropylol, the true homologue of chlorethylchloride, $CH_3—CHCl_2$. The corresponding bromopropylol is at present unknown, but there is no doubt that the action of phosphoric pentabromide on propylic aldehyde would yield it.

The author intends investigating the five chlorobromides of propylene, which theory indicates as capable of existing.

C. E. G.

Preparation of Glycols. By A. JELTEKOW (Deut. Chem. Ges. Ber., vi, 558).

On heating methylene bromide to 140°—150° in sealed tubes, with 15 or 20 times its volume of water and excess of lead oxide or carbonate, lead bromide is formed, together with ethylene glycol and traces of ethylene oxide. A similar reaction takes place with ethylene chloride at 170°. From these results the author infers that the formation of aldehyde by the action of water on ethylene bromide (*Ann. Chem. Pharm.*, cxxxi, 173) is due to the presence of free hydrobromic acid formed during the reaction.

Propylene bromide under similar circumstances yields acetone; and the propylene chloride boiling at 93° yields acetone, propylene glycol, and traces of a substance capable of reducing silver salts, probably propylene oxide or propylic aldehyde. From 24 grams of propylene chloride 2·5 grams of acetone and 5 grams of propylene glycol boiling between 185° and 186° were obtained. Acetone is formed, whether the mixture contains a free haloïd acid or not.

C. E. G.

Action of the principal Derivatives of Amylic Alcohol on Polarised Light. By J. PIERRE and E. PUCHOT (Compt. rend., lxxvi, 1332—1334).

THE authors have made a number of observations of the rotatory power possessed by the amyl alcohol of fermentation and its derivatives.

They set out by stating that in the course of these experiments they have never encountered the optically inactive alcohol of Pasteur.

They indicate, as a point worthy of attention, that the action of amylic alcohol upon polarised light being equal, though opposite, to that of a solution of cane sugar containing 1·4 per cent., its rotatory power is increased one-third by the addition of about 6 per cent. of water.

The following table includes the chief results obtained:—

	Density at 0°.	Boiling-point.	Rotation.
Amyl valerate....	·874	190°	+ 40°
Amyl butyrate	·8769	170·3°	+ 8·5°
Butyl valerate	·8884	173·4°	+ 3°
Propyl valerate	·8862	157°	+ 9°
Ethyl valerate	·886	135·5°	+ 12·5°
Methyl valerate................	·9005	117·5°	+ 8·5°
Valeric acid	·947	178°	+ 5°
Amyl alcohol (anhydrous)	·8255	130°	− 8·5°
Amyl alcohol, with 6 p.c. water ..	—	—	− 11°
Pure amyl aldehyde	·8209	92·5°	+ 6°
Crude amyl aldehyde	—	—	+ 18°

W. A. T.

On Amylic Alcohol.

By O. POPOFF (Deut. Chem. Ges. Ber., vi, 560).

THE author has found that amylic alcohol which, by fractional distillation, gives the powerfully polarising alcohol, if treated with alkali or a solution of calcium chloride previous to fractionation, no longer yields the optically active alcohol.

C. E. G.

Constitution of the Allyl Compounds. By AUG. KEKULÉ and A. RINNE (Deut. Chem. Ges. Ber., vi, 386—388).

NOTWITHSTANDING the strong evidence adduced by Kekulé, in support of the formula

$$CH_3—CH═CH—CO_2H$$

for crotonic acid from crotonic aldehyde many chemists still regard

$$CH_2═CH—CH_2—CO_2H$$

as the correct expression, in consequence of the formation of the acid

from allyl alcohol, which undoubtedly is correctly represented by the formula

$$CH_2{=}CH{-}CH_2(OH).$$

All observations with regard to the behaviour of allyl alcohol and crotonic acid lead, however, as already pointed out by Kekulé (this Journal, x, 618), to the conclusion that, at some stage of the conversion of the one into the other, an alteration in structure takes place. The authors consider that they have now experimentally demonstrated the correctness of this view. In the first place they show that the modification cannot be supposed to occur during the conversion of the alcohol into the iodide, since the alcohol regenerated from the allyl oxalate prepared with allyl iodide from pure allyl alcohol from glycerin, is in all respects identical with the alcohol employed in the preparation of the oxalate.

In the next place, the authors have oxidised allyl alcohol, iodide, and cyanide, employing both chromic and nitric acid as oxidants. Basing their deductions on the assumption that an allyl compound represented by the formula

$$CH_3{-}CH{=}CH.R$$

should yield acetic acid, whereas a compound of the formula

$$CH_2{=}CH{-}CH_2.R$$

cannot yield acetic acid, but may be expected to furnish formic acid and (with nitric acid as oxidant) oxalic acid, they find that their results are entirely confirmatory of the view that a change occurs during the formation of the cyanide, the iodide, $CH_2{-}CH{=}CH_2I$, yielding the cyanide, $CH_3{-}CH{=}CH(CN)$. Thus allyl alcohol gave with chromic acid some acrolein, together with formic acid and carbonic anhydride; with nitric acid, formic and oxalic acid—but in neither case acetic acid. Similarly, allyl iodide gave formic acid and carbonic anhydride, but no acetic acid. Allyl cyanide, however, readily gave acetic acid in quantity on oxidation both with chromic and nitric acids. To meet the possible objection that the cyanide is converted into crotonic acid, and that it is in reality the latter which is oxidised, the authors state that whereas crotonic acid is oxidised with great difficulty, allyl cyanide is most easily oxidised.

H. E. A.

The Dibromopropionic Acid obtained from Propionic Acid. By O. PHILIPPI and B. TOLLENS (Deut. Chem. Ges. Ber., vi, 515—519).

THE following three modifications of dibromopropionic acid are possible:—

I.	II.	III.
$CHBr_2$	CH_2Br	CH_3
CH_2	$CHBr$	CBr_2
$COOH$	$COOH$	$COOH.$

The (β) dibromopropionic acid obtained by Münder and Tollens from allyl bromide was shown to have the constitution represented by the formula II, and as the acid obtained by Friedel and Machuca cannot have the constitution I, this having been derived from mono-bromopropionic acid, in which the bromine is known to be united with the carbon standing next to the hydroxyl carbon, it follows that if the acid of Friedel and Machuca (α) can be definitely proved to be non-identical with that of Münder and Tollens, the former must have the constitution III.

The authors find that the acid of Friedel and Machuca is deliquescent when impure, but permanent when pure; consequently it may be purified by exposure to the air, the impure portions deliquescing and draining away. When pure it melts at 60°, and crystallises, on solidifying, in small quadratic tables, which are sometimes truncated.

One of the most remarkable distinctions between the α acid and the β acid is found in the fact that when a sample of either modification is melted, and a portion of the same kind is added, crystallisation takes place; but if a portion of the other modification is added, this becomes melted, and it remains fluid even after the solidification of the bulk of the sample. The α acid boils at 220°—221°, while the β acid does not distil completely below 240°, partial decomposition taking place. When the β acid is reduced by zinc and sulphuric acid, the product is acrylic acid, while the α modification yields propionic acid on reduction. Propionate of lead was found to be crystallisable, although with difficulty.

The salts of α dibromopropionic acid differ from those of the β salt. The *calcium salt*, $\alpha(C_3H_3Br_2O_2)_2Ca + 2H_2O$, forms fine lustrous needles, which lose their water at 90°. The *barium salt* $(C_3H_3Br_2O_2)_2Ba + 9H_2O$, forms needles similar to the calcium salt. The *ethylic ether* obtained by the action of hydrochloric acid on an alcoholic solution of the α acid, forms a liquid with a camphoric odour, having a specific gravity of 1·7536, and boiling at 190°—191°. The difference between the boiling point of this ether and that of the β ether is about 22°, or rather less than the difference between the boiling point of propylene bromide and that of methyl-bromacetol; consequently an analogous difference of constitution probably exists.

By boiling the α dibromopropionic acid with alcoholic potash, a crystallised potassium salt was obtained which, when treated with sulphuric acid, and agitated with ether, yielded an acid, melting at 69°—70°, and apparently identical with the acid similarly obtained from the β dibromopropionic acid.

T. B.

On the Action of Sodium-Amalgam on Dinitroheptylic Acid. By H. A. Kullhem (Ann. Chem. Pharm., clxvii, 45—48).

The author has described, under the name *dinitroheptylic acid*, a body which is obtained by boiling camphor for a long time with nitric acid.

By the action of sodium amalgam on the alcoholic solution of this body, a corresponding mononitroheptylic acid, $C_6H_{11}(NO_2)O_2$, is formed,

which furnishes a sodium salt, $C_6H_{10}(NO_2)NaO_2.3H_2O$, a barium salt $[C_6H_{10}(NO_2)O_2]_2Ba.3H_2O$, and a silver salt, $C_6H_{10}(NO_2)AgO_2$, all of which are crystallisable.

W. A. T.

Decomposition-products of the Chloranhydride of Glyceric Acid. By WERIGO and OKULITSH (*Ann. Chem. Pharm.*, clxvii, 49—62).

THE following appear to be the principal results obtained in this research, which, however, is at present incomplete.

The authors have examined the action of water and of alcohol under different conditions upon the product of the action of phosphorus pentachloride on glyceric acid.

When the decomposition by water was effected gradually, as by exposing the substance to a moist atmosphere, an acid was obtained, the lead salt of which had nearly the composition of a basic salt of chloropropionic acid. On the other hand, when poured into water, it furnished a mixture of two acids, one of which contained chlorine.

When in the preparation of the chloranhydride any notable rise of temperature is avoided, a product is obtained, which gives a clear solution when poured into water. But when gradually heated to 150°, the resulting compound gives with water a white thick syrup. This syrup gradually assumes the consistence of honey, and becomes transparent. The honey-like body decomposed by baryta-water furnished barium monochlorolactate.

The product of the decomposition of the chloranhydride by alcohol, submitted to fractional distillation, gave a colourless aromatic liquid, boiling between 185° and 190°, besides two other fractions having an oily consistence. The analysis of the principal product, although giving very discordant numbers, showed that it was probably ethyl dichloropropionate.

W. A. T.

Preparation of. Trimethylacetic Acid. By A. BUTLEROW (*Deut. Chem. Ges. Ber.*, vi, 564—565).

THE attempts to prepare trimethylacetonitril by the action of potassio-mercuric cyanide, $HgCy_2 2KCy$, on isobutyl iodide were unsuccessful; tertiary butyl iodide, however, is easily attacked, and the reaction proceeds at the ordinary temperature; addition of water to the product precipitates an oily mixture of *trimethyl-methylformamide* and *trimethyl-acetonitril;* the crystals of the latter melt at 15° to 16°, and it boils at 105° to 106°. The oil is heated to 100° in closed tubes, with concentrated hydrochloric acid, and the crude trimethylacetic acid thus obtained is purified by means of the potassium salt, and subsequently by fractional distillation. By this process tertiary butyl iodide yields 14 per cent. of the pure acid.

The author, by means of this acid, hopes to obtain trimethyl-ethyl alcohol, penta-methyl-ethyl alcohol, and trimethyl-methyl ketone, which he believes to be identical with pinacolin, since Friedel and Silva have

obtained from pinacolin alcohol, an acid which is apparently trimethyl-acetic acid. If this be the case, the following will be the constitutional formulæ of these compounds :—

$$\begin{array}{ccccc} (CH_3)_2C(HO) - H_2O & = & (CH_3)_3C + H_2 & = & (CH_3)_3C \\ | & & | & & | \\ (CH_3)_2C(HO) & & CH_3—CO & & CH_3—CH(HO). \\ \text{Pinacone.} & & \text{Pinacolin.} & & \end{array}$$

C. E. G.

Preparation and Properties of Oxymaleic Acid.

By E. BOURGOIN (Compt. rend., lxxvi, 1265—1267).

THIS acid is prepared from potassium monobromomaleate by the action of silver oxide on its cold aqueous solution. The new acid is then precipitated by lead acetate as a lead salt which is subsequently decomposed by sulphuretted hydrogen. On evaporating the solution and crystallising the product from ether, the oxymaleic acid is obtained in tufts of long, slender crystals which are very soluble in water, alcohol, and ether. Its silver salt has the composition $C_8H_4Ag_2O_{10}$, the acid being bibasic. The salts with the alkali-metals are crystalline and very soluble in water; the silver compound is a white precipitate soluble in acids and in ammonia; it is very unstable, detonating when strongly heated, and being decomposed by ebullition with water. Acetate of lead also yields an abundant precipitate of oxymaleate, which is soluble in nitric acid, but insoluble in the fixed alkalis and in ammonia. On boiling an aqueous solution of isobromosuccinic acid, the bromine is entirely eliminated as hydrobromic acid, producing an organic acid, which the author proposes to compare with oxymaleic acid.

C. E. G.

Preparation of Organic Sulpho-acids. By W. HEMILIAN (Deut. Chem. Ges. Ber., vi, 562—563).

THE author finds that ammonium sulphite is preferable to the potassium salt for the preparation of these acids, the reaction being very sharp when the haloid derivatives of the acids are boiled with an aqueous solution of the sulphite :—

$$RCl + (NH_4)_2SO_3 = NH_4Cl + R.NH_4.SO_3.$$

The free acid can readily be obtained from the product of the reaction by boiling it with lead oxide, and subsequently decomposing the lead salt by sulphuretted hydrogen. He has thus prepared α-sulphobutyric acid, $CH_3—CH_2—CH\langle{HSO_3 \atop HCO_2}$, from pure ethylic α-bromobutyrate, and finds it to be identical with that which he previously obtained by the action of chlorosulphuric acid, $HClSO_3$, on butyric acid, also with Hofmann's and Buckton's acid. The author has also prepared β-sulphobutyric acid, $CH_3—CH(HSO_3)—CH_2.CO_2H$, from ethylic β-chlorobutyrate. The latter, which boils at 150°—160°, was obtained from

the β-chlorobutyric chloride, formed by the action of phosphoric chloride on sodium β-oxybutyrate, CH_3—$CH(HO)$—$CH_2.CO_2Na$. Genther's ethyldiacetic acid being converted into β-oxybutyric acid by treatment with sodium-amalgam in the manner proposed by Wislicenus The new acid is a transparent hygroscopic, gum-like substance. Its lead, barium, and calcium salts do not crystallise, and are thrown down as flocculent precipitates on adding alcohol to their aqueous solutions. The barium compound obstinately retains one H_2O, which it parts with only at 200°, the salt at the same time becoming brown, and being partially decomposed.

C. E. G.

Action of Phosphorus Pentachloride on Sulphacetic Acid. By R. SIEMENS (Deut. Chem. Ges. Ber., vi, 659—662).

ACCORDING to Vogt, the chloride of sulphacetic acid yields by reduction thiacetic acid. But according to all analogy, thioglycollic acid ought to be formed, the more so as Carius, by acting with potassium monochloracetate on potassium sulphydrate, obtained a thioglycollic acid which by oxidation yielded sulphacetic acid. To clear up this point the following experiments were undertaken:—

1 mol. of sodium sulphacetate and 2 mols. of phosphorus pentachloride were gently heated. A quiet reaction took place and *monochlorosulphacetyl chloride* was formed, which was isolated by distilling the product *in vacuo*.

Monochlorosulphacetyl chloride is a colourless, limpid liquid, which fumes slightly in the air, and boils in Bunsen's vacuum, the column of mercury being 645 mm. at 130°—135°. Its composition is COCl—CHCl.SO_2Cl. By treating it with tin and hydrochloric acid it is converted into thioglycollic acid, which can also be obtained by this reaction from the crude product, only the reaction is much more violent. The barium and lead salts having the composition:—

$$\left.\begin{matrix} CH_2.S \\ | \\ CO.O \end{matrix}\right\} Ba \qquad\qquad \left.\begin{matrix} CH_2.S \\ | \\ CO.O \end{matrix}\right\} Pb,$$

were analysed. The barium salt forms microscopic crystals, and is soluble in water; the lead salt is an insoluble precipitate. This acid appears not to be identical with that obtained by Carius; the latter at least does not state that in his compound two atoms of hydrogen can be replaced by metals.

When the pure chloride is mixed with water, carbon dioxide is given off, a portion dissolves, and insoluble *trichloromethylsulphonic chloride*, $CCl_3.SO_2Cl$, is left behind, while the solution contains sulphacetic acid:—

$$3 \begin{matrix} CHCl.SO_2Cl \\ | \\ CO.Cl \end{matrix} + 5H_2O = 2 \begin{matrix} CH_2.SO_2.OH \\ | \\ CO.OH \end{matrix} + \begin{matrix} CCl_3 \\ | \\ SO_2Cl \end{matrix} + 5HCl + CO_2$$

It is possible, however, that the chloride was not a pure compound, but a mixture of:—

(1)	(2)	(3)
$CCl_2.SO_2Cl$	$CHCl.SO_2Cl$	$CH_2 SO_2Cl.$
|	|	|
$COCl$	$COCl$	$CO Cl.$

In this case the compound No. 1 would yield trichloromethylsulphonic chloride, carbon dioxide, and nascent hydrogen, which latter would reduce No. 2 to No. 3, and this normal chloride would then be resolved into sulphacetic acid and hydrochloric acid. To obtain the normal chloride, sodium sulphacetate was treated with phosphorus oxychloride, but without success, the product consisting apparently of an anhydride. C. S.

On Valeritrine. By H. LJUBAVIN (Deut. Chem. Ges. Ber., vi, 565—566).

THIS compound is produced by heating valeral with twice its volume of alcoholic ammonia to 150° for about 40 hours: $3C_5H_{10}O + NH_3 - 3H_2O = C_{15}H_{27}N$. In order to purify it, the uncrystallisable hydrochloric acid compound is decomposed by potassium hydrate, and the free base distilled off in a current of steam. Its alcoholic solution is then precipitated by picric acid, and the picrate, $C_{15}H_{27}N.C_6H_2(NO_2)_3O$, recrystallised from hot alcohol; it forms long yellow needles which melt at 129°—130°, and are sparingly soluble in cold alcohol, freely when it is warm. Valeral yields about 30 per cent. of this salt. The free base is a colourless mobile liquid which boils at 250°—260°, and when warm has an odour resembling conine. It is almost insoluble in water and in aqueous alkalis, but easily soluble in alcohol, in ether, and in the acids, forming salts, which as a rule do not crystallise, and are decomposed by boiling with aqueous solutions. The chloroplatinate, $2(C_{15}H_{27}N.HCl) PtCl_4$, crystallises in orange-coloured granules, which are easily soluble in alcohol, but only sparingly in ether or water. Mercuric chloride yields a double salt, $C_{15}H_{27}N.HCl + HgCl_2$, in rhombohedral crystals, which melt at 86°—88°, and are soluble in boiling alcohol. Sodium has no action on valeritrine even at 250°.

C. E. G.

The Metallic Derivatives and Constitutional Formula of Cyanamide. By E. MULDER (Deut. Chem. Ges. Ber., vi, 655—658).

THE author was in hopes of being able to synthethise glycoluril, $C_4H_6N_4O_2$, by the action of bromacetylurea on cyanamide, but at 105°, in presence of ether, he only obtained a gelatinous substance insoluble in water.

The addition of silver nitrate or of an ammoniacal solution of silver nitrate to an aqueous solution of cyanamide, produces a yellow precipitate, which, when suspended in ether and decomposed by sulphuretted hydrogen, is reconverted into cyanamide; from this the author concludes that the formula of the latter is $C\begin{cases}NH\\NH\end{cases}$ and not $N\equiv C-NH_2$, and proposes to call it *cardimide* or *carbodiimide;* he draws attention to the fact that by this means the formation of guanidine by the action

of ammonia, and of glycocyamine by union with glycocine admits of a simple explanation, as do also its transformation into urea—

$$C{<}^{NH}_{NH} + H_2O = CO{<}^{NH_2}_{NH_2}$$

and into dicyanodiamide,

$$\begin{matrix} NH{=}C{=}NH \\ \\ HN{=}C{=}NH \\ \text{2 mol. carbodiimide.} \end{matrix} = \begin{matrix} HN{=}C{<}^{NH}_{NH}{>}C{=}NH \\ \text{Dicyanodiamide.} \end{matrix}$$

The silver carbodiimide is insoluble in water, slightly soluble in ammonia, but soluble in dilute nitric acid, and reprecipitated by ammonia as potassium hydrate; it is not decomposed by boiling with the latter, or by exposure to light. It undergoes no change at 220°, but at a higher temperature it explodes, with formation of cyanogen,

$$AgN{=}C{=}NAg = 2Ag + N + CN.$$

Cyanamide is precipitated by ammoniacal cupric sulphate, but creatine gives no compounds corresponding with those of cyanamide. The author concludes with some theoretical speculations on the constitution of glycoluril, suggesting the formula—

$$NH_2—CO—NH—CO—CH_2—N{=}C{=}NH.$$

C. E. G.

Addition-products of Cyanamide. By E. Baumann (Ann. Chem. Pharm., clxvii, 77—86).

Ethyl carbamate (urethane) and cyanamide do not combine when heated together, either in the dry state or in an aqueous or alcoholic solution. From this it seems probable that in the formation of creatine from sarcosine and cyanamide, the latter combines with the carboxyl and not with the amido-group.

According to Strecker, alanine combines with cyanamide, but he has not described the compound, which is isomeric with creatine, and may be called *Alacreatine*, $C_4H_9N_3O_2$. It is obtained by adding a little ammonia to a concentrated aqueous solution of the bodies and leaving the mixture to stand; first dicyanamide crystallises out, and then the new compound. The yield of it increases by employing an excess of alanine, but never approaches the theoretical amount.

It forms prismatic anhydrous crystals, resembling creatine; it is almost insoluble in cold alcohol and very sparingly in hot alcohol, but freely in water; dissolving in 12 parts at 15°, whilst, according to Liebig, creatine requires 74 parts at 18°. By heating it to 170°—180°, or treating it with dilute sulphuric acid, it loses water and is converted into *alacreatinine*, which dissolves in water and alcohol more freely than alacreatine.

From an aqueous solution it crystallises in long needles resembling urea, and from alcohol in small rhombohedral anhydrous crystals, which in the air absorb water and change into needles. It is a base resembling creatinine, forming double salts with zinc chloride and other chlorides.

It also reduces mercuric oxide; yielding a strongly alkaline base and other products, but no oxalic acid.

C. S.

Oxidation of Allantoïn with Ferricyanide of Potassium.

By F. C. E. van Embden (Ann. Chem. Pharm., clxvii, 39—45).

Lantanuric acid is a body which, according to Schlieper, is produced by the oxidation of allantoin with ferricyanide of potassium in presence of potash. Mulder some time ago (*J. Chem. Soc.* [2], ix, 1197) found that an entirely different substance was formed by this process, and from this result the author was led to make a further examination of the reaction.

A solution of allantoin in caustic potash was mixed with solution of potassium ferricyanide. A coloration was at first produced, but soon disappeared, and continued to do so until just one molecule of $K_6Fe_2Cy_{12}$ had been added for every molecule of allantoin $C_4N_4H_6O_3$ present. The liquid then acidified with acetic acid, deposited a crystalline precipitate which was crystallised from hot water and analysed. The aqueous solution of this compound had an acid reaction. It gave white precipitates with lead acetate, with silver nitrate, and with baryta-water. It lost no water by exposure over sulphuric acid or at 100°. Analysis showed it to be the acid potassium salt of a new dibasic acid, *allantoxanic acid*, represented by the formula, $C_4N_3H_3O_4$.

The same body is produced when, instead of allantoin, potassium allantoate is submitted to the same process of oxidation.

Neutral allantoxanate of lead is $C_4N_3HPbO_4$; the silver salt is $C_4N_3H_2AgO_4$; an unstable barium salt has the composition $C_4N_3HBaO_4$.

The acid itself, obtained from the lead salt by means either of sulphuretted hydrogen or of sulphuric acid, although capable of crystallising, is exceedingly unstable, the solutions evolving carbon dioxide even at ordinary temperatures.

The formation of the new acid from allantoin is represented in the following equation:—

$$\underset{\text{Allantoin.}}{C_4N_4H_6O_3} + O = \underset{\text{Allantoxanic acid.}}{C_4N_3H_3O_4} + NH_3.$$

W. A. T.

A Supposed Isomeride of Piperidine, obtained from the Nitro-derivative of a Member of the Group C_nH_{2n}. By H. Gal (Compt. rend., lxxvi, 1354—1356).

No nitro-derivative of the hydrocarbon group C_nH_{2n} has yet been described. The author has obtained one of them as follows. Nitrethane was treated with the quantity of alcoholic potash necessary to convert it into potassium nitrethane, and then with its equivalent of allyl iodide. The reaction was very energetic, potassium iodide was precipitated, and, on adding water to the filtered liquid, an oil was obtained

having a formula which is that of the nitro-derivative of Wurtz's ethyl-allyl, or of amylene. The reaction is probably thus:—

$$C_2H_4KNO_2 + C_3H_5I = KI + C_5H_9NO_2.$$

The new nitro-derivative could not be purified for analysis, since it is decomposed by distillation. The crude product when reduced by nascent hydrogen lost its oily character, and, upon distillation with excess of potash, a colourless, strongly alkaline liquid was obtained, from which potash separated a base having the odour of piperidine. It is soluble in water and in alcohol. Its chloroplatinate appears in the form of brilliant yellow plates, having the same percentage of platinum as piperidine chloroplatinate. On the other hand, its boiling point is 85°, that of piperidine being 106°, and, although, like piperidine, it reacts energetically with carbon sulphide, no crystals are obtained on cooling the liquid, as is the case with that base. Though scarcity of material has prevented the author from making a full examination of this substance, he believes it to be a primary monamine, having the formula $\left.\begin{matrix}C_5H_9\\H\\H\end{matrix}\right\}N$.

B. J. G.

Aromatic Compounds containing Silicium. By A. Ladenburg (Deut. Chem. Ges. Ber., vi, 379).

Silicium phenyltrichloride, $SiC_6H_5Cl_3$, is prepared by heating mercury-phenyl with silicium chloride in sealed tubes at 300°, the product being separated by fractional distillation. It is a colourless liquid boiling at 197°, which fumes in the air and is slowly decomposed by cold water, more rapidly, however, on warming or on addition of ammonia. On treatment with alcohol it yields *orthosilicobenzoic ether*, $SiC_6H_5(OC_2H_5)_3$, which is a colourless liquid boiling at 237°, of sp. gr. 1·0133 at 0°, and 1·0055 at 10°; aqueous hydriodic acid converts this ether into silicobenzoic acid. The author has also obtained *silicobenzoic anhydride* $(SiC_6H_5O)_2O$, in the form of an amorphous colourless substance, moderately soluble in ether, less soluble in alcohol, and but very slightly soluble in water; it is readily soluble in aqueous potash, the addition of hydrochloric acid to this solution producing no precipitate, but on the addition of an excess of ammonia silicobenzoic acid is at once thrown down. When heated with potassium hydrate, the anhydride furnishes benzene.

H. E. A.

Action of Phenol and Caustic Potash on Dinitrochlorobenzene. By A. Maikopar (Deut. Chem. Ges. Ber., vi, 564).

The author finds that the action of an alcoholic solution of potash and phenol on dinitrochlorobenzene gives rise to an ether of the composition, $C_6H_3(NO_2)_2.C_6H_5O$. It crystallises in scales which melt at 65°; they are resolved by the action of potassium hydrate into phenol and the potassium-compound of dinitrophenol. The sulphonic acid prepared

from this ether is not identical with the acid discovered by Glutz. The author also states that benzene occurs amongst the products of the action of phosphoric anhydride on phenol.

C. E. G.

Derivatives of Monoxy-azobenzene. By TSCHIRVINSKY (Deut. Chem. Ges. Ber., vi, 560—561).

PURE *monoxy-azobenzene* crystallises in brick-red rhombic prisms, which melt at 150°, and are soluble in toluene and in dilute alcohol, sparingly in boiling water. The addition of silver nitrate to its ammoniacal solution produces a flocculent precipitate which becomes crystalline on standing. The action of nitric acid converts monoxy-azobenzene into picric acid. *Benzoxy-azobenzene*, $C_{12}H_9N_2O(C_7H_5O)$, crystallises in plates or tetrahedrons which melt at 136°, and are easily soluble in toluene, less so in ether, and sparingly in alcohol. *Monosulphoxy-azobenzolic acid*, $C_{12}H_9N_2O(HSO_3)$, prepared by the action of fuming sulphuric acid on oxyazobenzene, crystallises in well-formed octohedrons, which are easily soluble in water. The barium compound crystallises in golden-yellow scales, containing 2 molecules of water. The easily soluble copper and magnesium compound crystallise with $3H_2O$; the potassium salt is anhydrous.

C. E. G.

The Azo-derivatives of Liquid and Solid Nitrotoluene. By H. PETRIEFF (Chem. Ges. Ber., vi, 556—558).

PURE *β-azotoluene* can be obtained only by the oxidation of the corresponding hydro-compound; it melts at 144°—145°, and sublimes undecomposed. It is more difficultly soluble than α-azotoluene. *β-mononitroazotoluene* melting at 76°, and *β-dinitroazotoluene* melting at 110°, are obtained by gently heating β-azotoluene with nitric acid of sp. gr. 1·4. The dinitroazotoluene crystallises out first in yellow needles from the alcoholic solution of the product, colourless needles of the mononitro-compound being obtained from the mother-liquors. Strong nitric acid (1·34) converts β-azotoluene into *trinitroazoxytoluene*, melting at 201°, and identical with that formerly obtained from α-azotoluene. *β-monobromoazotoluene*, melting at 136°, can be prepared by the direct action of bromine on the corresponding azotoluene. It crystallises in tufts of needles, which are difficultly soluble in alcohol or ether, but readily in chloroform and benzene. It sublimes unchanged.

β-mononitroazoxytoluene, melting at 84°, and *β-dinitroazoxytoluene*, melting at 145°, are obtained by gently heating β-azoxytoluene (melting point 59°), with nitric acid of density 1·4. They both crystallise in yellow needles, and can be separated by taking advantage of the difference in their solubilities in alcohol, in which the dinitro-compound is insoluble. Strong nitric acid yields trinitroazoxytoluene. *β-dibromoazoxytoluene* is obtained on dissolving β-azoxytoluene in bromine; it crystallises in needles which melt at 138°, and are but sparingly soluble in alcohol.

Dry α-hydrazotoluene, melting at 165°, can be kept unchanged if not exposed to the air, but is converted into azotoluene and azoxytoluene by contact with alcohol or water, and more quickly when boiled with alcoholic potash, or with animal charcoal. Nitrous acid changes it entirely into azoxytoluene. On passing dry hypochlorous acid into an ethereal solution of α-hydrazotoluene, a white powder is obtained, easily soluble in water; this solution gives, with silver and copper nitrates, insoluble precipitates which, when treated with an alkali, yield a substance crystallising in nacreous scales melting at 112°. This substance is difficultly soluble in water, easily in alcohol or ether, and from the composition of its hydrochloride, $C_{14}H_{16}N_2.2HCl$, would appear to be an isomeric tolidine. Beside the white compound previously mentioned, the action of hypochlorous acid also yields azoxytoluene and an addition-product: $C_{14}H_{16}N_2Cl_2O.3C_{14}H_{16}N_2 + 2Cl_2O = C_{14}H_{16}N_2\,2HCl + C_{14}H_{16}N_2Cl_2O + C_{14}H_{14}N_2O$.

Azoxybenzene is obtained when a solution of azobenzene in acetic acid is heated with chromic anhydride to 150°—250° in sealed tubes. Repeated treatment with boiling nitric acid (density 1·54), converts azobenzene into trinitroazoxybenzene, which crystallises in long needles, whilst the addition of water to the mother-liquors causes the separation of a resinous mass which crystallises from alcohol in long yellow needles, melting at 85°, and having the composition of dinitrobenzene. *Dioxytrinitroazobenzene* (oxytrinitroazoxybenzene), $C_{12}H_7(NO_2)_3N_2O_2$, is obtained by heating a solution of trinitroazoxybenzene in concentrated nitric acid with chromic anhydride for 12 hours to 180°—200° in closed tubes; the product is precipitated by water, washed with ether and alcohol, and finally crystallised from nitric acid, benzene, or chloroform. It forms slender needles which melt at 102°. By the further action of the oxidising mixture, *trioxytrinitroazobenzene*, $C_{12}H_7(NO_2)_3N_2O_3$, is produced; it is a yellow crystalline mass which melts at 52°, and explodes when heated; it is easily soluble in chloroform or ether.

C. E. G.

Action of Bromine on Boiling Ethylbenzene.

By B. RADZISZEWSKI (Deut. Chem. Ges. Ber., vi, 492—494).

ATTEMPTS to prepare bromethylbenzene (styryl bromide) by Berthelot's method were unsuccessful, the product decomposing during distillation; but it was obtained in a tolerably pure state by treating ethylbenzene heated to 140° with a slight excess of bromine, washing the product, and refrigerating, in order to cause the dibromstyrol to crystallise out. From this substance styrylic alcohol was obtained, and the author intends to study the products of the oxidation of this alcohol.

By treating ethylbenzene, heated to 145°—150°, with two molecules of bromine, a crystalline compound having the composition $C_8H_8Br_2$ was obtained. It crystallises from ether in white needles or leaflets melting at 68°—69°. It decomposes spontaneously, becoming dark coloured, but it may be preserved under water without undergoing change, even though exposed to the light of the sun. When it is heated with water to 190°, no aldehyde of phenylacetic acid is formed, but hydrobromic acid and a bromstyrol having an agreeable odour.

These reactions show it to be identical with dibromstyrol, C_6H_5—$CHBr$—CH_2Br. When passed over lime heated to dull redness, it yielded a hydrocarbon having the composition C_8H_6, and boiling at 140°, which was found to be identical with Glaser's acetenylbenzene, also a crystalline hydrocarbon which appeared to be identical with the polystyrol of Engler and Leist.

By treating a mixture of bromethylbenzene and ethylbenzene with zinc, a hydrocarbon having the composition C_6H_5—C_2H_4—C_6H_5—C_2H_5 was obtained. The action of heat on this hydrocarbon, and the action of water, at a high temperature on bromethylbenzene are now being investigated by the author, the action in the latter case being different from that of water on benzyl chloride.

T. B.

Synthesis of Phenyl-allyl. By C. Chojnacki (Compt. rend., lxxvi, 1413).

By heating to 100°, under pressure, a mixture of equal parts of benzene and iodide or bromide of allyl with a fifth of its weight of zinc-powder, hydrobromic acid is disengaged, and a dark-coloured oil is obtained. By submitting this oil to distillation, the excess of benzene and allyl bromide separate, and between 130° and 160° the phenyl-allyl passes over. This hydrocarbon boils at 155°, and forms a limpid oil of agreeable odour. It gave satisfactory analytical numbers.

W. A. T.

Sulphur Derivatives of Cymene. By A. P. Flesch (Deut. Chem. Ges. Ber., vi, 478—482).

When cymene is prepared by the distillation of camphor with phosphoric sulphide, various compounds soluble in alkalis are formed in small quantity, and in order to free these portions from hydrocarbons, their alkaline solution was either agitated with ether or subjected to the action of a current of steam; afterwards the solution was acidified with hydrochloric acid, and the oil which separated was subjected to fractionation. The principal product was *cymene mercaptan*, $C_{10}H_{13}SH$. This substance forms a colourless liquid boiling at 235°—236°. It has a peculiar aromatic odour, is miscible with alcohol, but insoluble in water, and its specific gravity was found to be 0·9975. The *mercury compound*, $Hg(C_{10}H_{13})_2S_2$, which forms long bright needles, is prepared by boiling an alcoholic solution of the mercaptan with mercuric oxide and cooling the liquid; or as a white precipitate on mixing an excess of an alcoholic solution of the mercaptan with mercuric chloride. On distillation it yields metallic mercury, mercuric sulphide, and an oil which appears to be a mixture of cymene sulphide and disulphide. If an alcoholic solution of cymene mercaptan be added to excess of mercuric chloride, a more soluble compound, $C_{10}H_{13}S.HgCl$, is formed. The *silver compound*, $C_{10}H_{13}.S.Ag$, is obtained as a yellow crystalline precipitate by adding an excess of solution of the mercaptan to a solution of silver nitrate. If the mercaptan is not in excess, the

compound, $C_{10}H_{13}.S.Ag.AgNO_3$, is obtained. It crystallises from alcohol in leaflets.

Oxidising agents transform cymene mercaptan into cymene disulphide $(C_{10}H_{13})_2S_2$. This substance is best obtained by dissolving the mercaptan in an alkali and adding iodine, it then separates as an oil, which does not solidify on refrigeration.

When cymene mercaptan or cymene disulphide is treated with nitric acid, two atoms of carbon are eliminated, and sulphotoluic acid is formed. This acid crystallises in long thin hydrated prisms. Its *potassium salt*, $C_6H_3.CH_3.CO_2H.SO_3K$, forms prisms containing $3H_2O$. The *lead salt*, $C_6H_3.CH_3.CO_2.SO_3Pb + 3H_2O$, is deposited as a nodular crust when its aqueous solution is evaporated. When the salts are fused with potassium hydrate, two acids are formed; the more soluble of them, when purified by sublimation, melted at 202°—203°, and gave numbers agreeing with the formula of oxytoluic acid, but it differs from the known acids of this composition, by giving a violet colour with ferric chloride. The less soluble acid was purified by repeated solution in an alkali and precipitation by an acid, and it gave numbers corresponding more nearly with the formula of dioxybenzoic acid than with that of oxyterephthalic acid, but as the analysis of its calcium salt gave results corresponding more nearly with the formula of the latter, the author considers it probable that oxyterephthalic acid is really formed.

T. B.

Oxycymene and Thiocymene. By F. Roderburg (Deut. Chem. Ges. Ber., vi, 669—670).

The *oxycymene* (or cymic phenol) which H. Müller and Pott prepared by fusing cymene-sulphonic acid with potash, yields by distillation with phosphorus sulphide a thiocymene (or cymene mercaptan) identical with that which is obtained as a bye-product in the preparation of cymene from camphor. The same compound is formed by acting with nascent hydrogen on cymene-sulphonic chloride, and Kekulé and Fleisher obtained it by acting on camphor with iodine, and converting the oxycymene thus formed into thiocymene by means of phosphorus sulphide.

These experiments show that in cymene-sulphonic acid, as well as in oxycymene and thiocymene derived from it, the inorganic groups occupy the same position as in oxycymene and thiocymene, which are prepared directly from camphor.

When thiobenzene is fused with potash, some phenol is formed. Thiocymene from camphor did not yield oxycymene by this reaction.

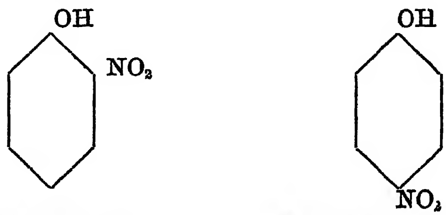
C. S.

Isomeric Dinitrophenols. By H. Huebner and W. Schneider (Ann. Chem. Pharm., clxvii, 89—117).

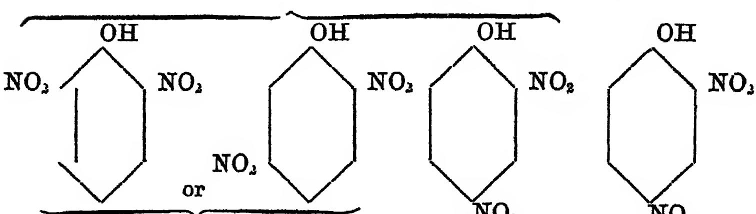
The authors enter at length into all the details of the preparation and properties of α- and β-dinitrophenol and their metallic derivatives. An abstract of their preliminary communication has, however, already

been given (this Journal, x, 483), which contains the substance of the present communication, excepting the discussion on the constitution of the nitrophenols. They remark, in the first place, that with regard to the mononitrophenols, there is as yet no experimental evidence to show what is the position occupied by the nitro-group relatively to the hydroxyl-group, and that therefore theoretical considerations alone are available in the discussion. Judging, however, from the circumstances attending their formation, and from their physical properties as compared with the physical properties of other di-derivatives of known constitution, they are of opinion that whereas in the one (volatile nitrophenol) the nitro-group occupies the position 2, in the other (non-volatile nitrophenol) that group probably occupies the position 4, since on this supposition alone is it explicable that but a single dinitrophenol is formed from it on nitration.

In the conversion of the mono- into di-nitrophenols, when it is considered that the presence of a nitro-group opposes the introduction of new negative constituents[*] (NO_3, Cl, Br) it follows that the second nitro-group will take up a position remote from the first, as represented by the following formulæ :—



Volatile nitrophenol. Non-volatile nitrophenol.



β-Dinitrophenol. α-Dinitrophenol.

H. E. A.

Action of Ozone on Pyrogallic Acid. By J. D. BOEKE (Deut. Chem. Ges. Ber., vi, 486—488).

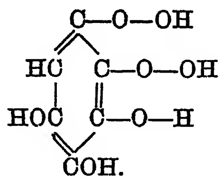
ONE molecule of pyrogallic acid and three molecules of potassium hydrate were dissolved in water and exposed to the action of ozonised oxygen until the dark colour first produced had given place to a reddish

[*] Nitro-benzoic acid is less easily converted into dinitrobenzoic acid than is benzoic into nitrobenzoic acid; the presence of a nitro-group in benzene entirely prevents the introduction of chlorine, bromine, or iodine.

yellow tint. The product possessed an odour recalling that of the fatty acids, and titration showed that two-thirds of the potash had been neutralised by the products of the oxidation. After neutralisation with acetic acid, the solution was precipitated by lead acetate, and the precipitate was decomposed by means of hydrosulphuric acid. The lead sulphide resulting from this decomposition was found to yield to alcohol a small quantity of a substance having an odour like that of a volatile fatty acid. The aqueous liquid, filtered from the lead sulphide, was nearly neutralised with baryta-water, when a gelatinous precipitate was deposited, and on the application of heat to the filtrate from this, renewed precipitation took place. The barium salt first deposited gave numbers corresponding with the formula $C_6H_4BaO_7$, and the barium salt deposited on warming the above-mentioned filtrate appeared to be identical with this.

The solution from which the above-mentioned precipitates had separated was treated with the quantity of sulphuric acid required to separate the barium, and it yielded on evaporation a strongly acid syrup, in which small colourless crystals gradually formed. This acid gave numbers corresponding with the formula $C_6H_6O_7$.

These researches lead the author to assume the position 1 : 2 : 4 or 1 : 2 : 5 for pyrogallic acid, and the following formula for the new acid; but before giving a decided opinion, he intends to investigate the new substances more fully:—



T. B.

On a Compound $C_{14}H_8S_2$. By H. LIMPRICHT (Deut. Chem. Ges. Ber., vi, 534).

WHEN monochlorobenzyl sulphide is subjected to dry distillation, the following reaction takes place:—

$$2(C_6H_4Cl.CH_2)_2S = C_{14}H_8S_2 + 2(C_6H_4Cl.CH_3) + 2HCl.$$

The compound $C_{14}H_8S_2$ forms small, light, glistening, white plates, melting at 208°; it is sparingly soluble in cold, more readily in hot alcohol, and freely in ether, benzene, and carbon sulphide. With picric acid it forms the compound $C_{14}H_8S_2 + 2C_6H_2(NO_2)_3OH$, crystallising from benzene in small yellowish-red needles melting at 146°. Boiling water or alcohol decomposes it. On heating the original compound with bromine and a little water to 180°, it is converted into $C_{14}H_6Br_2S_2$; white crystalline crusts, which do not dissolve readily in any liquid except boiling xylene, and do not melt at 250°. The original compound

is completely burnt by acetic acid and chromic trioxide; nitric acid converts it into a yellow crystalline nitro-compound, and hydrochloric acid and potassium chlorate convert it into $C_{14}H_5Cl_3S_2$, which does not crystallise well. When the compound $C_{14}H_8S_2$ is dissolved in benzene, and sodium amalgam and hydrochloric acid are added, the body $C_{14}H_{10}S$ is formed in small flat needles melting at 143°—144°. This compound has great resemblance to *tolallyl sulphide*, $C_{28}H_{20}S_2$, and is perhaps identical with it. In this case the original compound would be $C_{28}H_{16}S_4$.

C. S.

Derivatives of Coerulignone. By C. Liebermann (Deut. Chem. Ges. Ber., vi, 381—386).

The author corrects the formula $C_{15}H_{14}O_6$ for coerulignone (this Journal, xi, 70) to $C_{16}H_{16}O_6$; that of hydrocoerulignone to $C_{16}H_{18}O_6$.

Hydrocoerulignone, he finds, contains two replaceable hydrogen atoms, the addition of potassium ethylate to an alcoholic solution of hydrocoerulignone producing an egg-yellow precipitate, $C_{16}H_{16}K_2O_6$, and sodium ethylate a similar precipitate, $C_{16}H_{16}Na_2O_6$. The acetyl derivative, $C_{16}H_{16}(C_2H_3O)_2O_6$, forms white crystals difficultly soluble in alcohol, which melt at 216°. *Benzoyl-hydrocoerulignone*, $C_{16}H_{16}(C_7H_5O)_2O_6$, crystallises in forms resembling sublimed benzoic acid, difficultly soluble in alcohol. It melts at 214°. It is obtained either by the action of benzoic chloride, or by treating the hydro-compound with benzoic anhydride at 150°—160° in an open flask in an oil-bath, a mode of procedure which is doubtless of universal application.

On heating hydrocoerulignone with hydrochloric acid in sealed tubes, methyl chloride and a body of the composition $C_{12}H_{10}O_6$ (*hexoxydiphenyl*) are the products. Hexoxydiphenyl crystallises in magnificent, glistening, colourless, rosette-like groups, and is soluble in most solvents; the solution in alkalis has a magnificent purple colour, which appears, however, to be the result of oxidation. It yields violet to blue, unstable precipitates with the metallic acetates, that produced by cadmium acetate being the most beautifully coloured. A crystalline hexacetyl derivative, $C_{12}H_4(C_2H_3O)_6O_6$, and the propionyl derivative, $C_{12}H_4(C_3H_5O)_6O_6$, were obtained; the benzoyl and isobutyryl derivatives could not be obtained pure. Hexoxydiphenyl is decomposed when passed over heated zinc dust, yielding diphenyl.

The author regards hexoxydiphenyl as a *dipyrogallol*—

$$\begin{cases} C_6H_2(OH)_3 \\ C_6H_2(OH)_3 \end{cases};$$

and hydrocoerulignone as its tetramethyl derivative—

$$\begin{cases} C_6H_2(OH)(OCH_3)_2 \\ C_6H_2(OH)(OCH_3)_2. \end{cases}$$

Whether coerulignone is the quinone or quinhydrone of hydrocoerulignone has not been determined.

In conclusion the author refers to some attempts made to ascertain

to which constituent of wood coerulignone owes its origin. None was obtained by distillation of pure cellulose (Swedish filter-paper or unbleached calico). The distillate from 2 lbs. of oak-bark contained doubtful traces, but from 2 lbs. of beech-wood no less than half a gram of pure coerulignone was isolated, thus showing that it is derived from some peculiar constituent of beech-wood.

H. E. A.

Synthesis of Carbazol.

By C. GRAEBE (Ann. Chem. Pharm., clxvii, 125—130).

WHEN aniline is passed slowly through a red-hot porcelain tube, it yields hydrogen, prussic acid, ammonia, a base boiling higher than aniline, and a small quantity of carbazol:—

$$2(C_6H_5.NH_2) = C_{12}H_9N + 2H + NH_3.$$

It seems that Hofmann has already obtained carbazol by this reaction (*Jahresb.*, 1862, 235) A better yield (about 10 per cent.) is obtained by using diphenylamine:—

$$\begin{matrix} C_6H_5 \\ C_6H_5 \end{matrix}\Big\rangle NH = \begin{matrix} C_6H_4 \\ | \\ C_6H_4 \end{matrix}\Big\rangle NH + 2H.$$

That carbazol is really imidodiphenyl is proved by the fact that by acting on it with acetic anhydride one atom of hydrogen is replaced by one of acetyl. Heated with hydriodic acid to 300° it yields the hydrocarbon $C_{12}H_{20}$.

C. S.

Derivatives of Naphthalene Tetrachloride. By E. GRIMAUX (Compt. rend., lxxvi, 575—578).

THE author has already shown that naphthalene tetrachloride when boiled is converted into a sort of glycol, $C_{10}H_6Cl_2(OH)_2$, to which he gives the name *dichloronaphthydrenic glycol.*

When a solution of this substance is distilled with zinc-powder, white needles are obtained consisting of α-naphthol, $C_{10}H_7OH$, which has hitherto been obtained by fusing the sulphonaphthalates with potash.

The action of alkalis on the body $C_{10}H_6Cl_2(OH)_2$ yielded only resinous products.

An attempt was therefore made to remove the chlorine by the action of water at a high temperature. The whole of the chlorine was separated as hydrochloric acid, and a resin was obtained accompanied by a crystalline body which appeared to be *oxynaphthol* or *hydronaphthoquinone*. It is so easily decomposible, however, that it could not be obtained in a satisfactory condition for analysis.

W. A. T.

Synthesis of Aromatic Ketones. By M. KOLLARITS and V. MERZ (Deut. Chem. Ges. Ber., vi, 536—548).

THE authors have already shown that by heating a mixture of benzene and benzoic acid with phosphorus pentoxide, diphenyl ketone is produced. The same compound is also formed by using benzoic anhydride in place of benzoic acid, and the phosphoric anhydride may be replaced by metaphosphoric and even by pyrophosphoric acid, the yield in the latter case being, however, but small. Boron trioxide and dry hydrochloric acid do not act on benzene and benzoic acid, even at 250°.

Tolylphenyl ketone, $C_7H_7.CO.C_6H_5$, is obtained by heating toluene with benzoic acid and phosphorus pentoxide to 180°—200° for 8—10 hours. It is first obtained as an oily liquid, from which after some time long pointed plates separate out, which crystallise from a mixture of ether and petroleum naphtha in large thick prisms resembling cœlestine, and melting at 56·5°—57°. It is readily soluble in ether and benzene, sparingly in petroleum naphtha, and little more freely in alcohol. By oxidation with chromic acid it yields benzoyl-benzoic acid, and therefore appears to be identical with Zincke's tolylphenyl ketone, although the latter compound is, according to this chemist, an oily liquid. When the solid ketone is heated with soda-lime to 250°—270° it is resolved into *benzene* and *paratoluic acid*—

$$CO\left\{\begin{matrix}C_6H_4.CH_3\\C_6H_5\end{matrix}\right. + NaOH = C_6H_6 + C_6H_4\left\{\begin{matrix}CH_3\\CO.ONa.\end{matrix}\right.$$

The portion of the ketone which remains liquid on standing yields also a large quantity of paratoluic acid; orthotoluic acid could not be detected.

α- and β-Naphthylphenyl ketone, $C_{10}H_7\,CO.C_6H_5$.—These two isomerides are formed together by heating naphthalene with benzoic acid and phosphorus pentoxide for 10—12 hours to 200°—220°. The α-compound crystallises from a mixture of ether and alcohol in thick short prisms melting at 77·5°, and the β-compound forms needles melting at 82°. By separating the two kinds of crystals mechanically and recrystallising them, they may be obtained pure. When α-naphthoic acid is heated with benzene and phosphorus pentoxide, only a small quantity of the α-ketone is produced, besides carbon dioxide, naphthalene, and *α-dinaphthyl ketone*. The latter compound is a glassy mass, which by recrystallisation first from a mixture of ether and alcohol, and finally from alcohol alone, yields colourless pointed needles melting at 135° and distilling without decomposition. It is also produced by heating naphthalene with α-naphthoic acid and phosphorus pentoxide. β-naphthoic acid and benzene give a good yield of β-naphthylphenyl ketone. *β-dinaphthyl ketone* is formed by heating β-naphthoëic acid with naphthalene and phosphorus pentoxide to 200°—220° for 20 hours. It crystallises from hot alcohol in plates, which soon separate into needles. It is less soluble in alcohol than the α-compound, and melts at 134·5°—135°. According to theory three dinaphthyl ketones may exist. The third modification appears to be

formed, as Mr. Gianoli Giuseppe has found, by distilling a mixture of potassium β-naphthalenesulphonate and oxalate. It melts at 140°.

Cymylphenyl ketone, $C_{10}H_{13}.CO.C_6H_5$, is obtained in small quantity only by heating camphor cymene with benzoic acid and phosphorus pentoxide. It is a pale yellow oil, possessing a very agreeable odour, and boiling at about 340°. It does not solidify in a freezing mixture, but becomes very viscid.

Chlorodiphenyl ketone, $C_6H_4Cl.CO.C_6H_5$, was prepared from chlorobenzene. It crystallises from a mixture of ether and alcohol in flat needles resembling benzoic acid, and from petroleum naphtha in needles grouped in globular masses, melting at 75·5°—76° and boiling above 300°.

Bromodiphenyl ketone, $C_6H_4Br.CO.C_6H_5$, is obtained from bromobenzene, and has great resemblance to the preceding compound. It melts at 81·5°.

Benzonitrile, benzoic acid, and phosphorus pentoxide did not yield a ketone, the nitrile being converted into the polymeric cyaphenine. When benzoic acid is heated with phosphorus pentoxide alone, no benzoyl-benzoic acid is formed, but a carbonaceous mass. Acetic acid, benzene, and phosphorus pentoxide did not yield methyl-phenyl ketone. Gases containing carbon dioxide were formed, and a small quantity of a liquid consisting probably of diphenyl ketone.

C. S.

Action of Ammonia and its Derivatives on Ketones in presence of Dehydrating Agents. By C. ENGLER and H. HEINE (Deut. Chem. Ges. Ber., vi, 638—643).

WHEN boiling acetophenone is acted upon by dry ammonia and phosphorus pentoxide, and the product distilled, a thick oil passes over first, and then a crystalline substance, which is partially soluble in hydrochloric acid. Ammonia precipitates from this solution *acetophenonine*, crystallising from hot alcohol in fine interlaced needles melting at 130°. The formula of this body is either $C_{48}H_{38}N_2$ or $C_{24}H_{19}N$. It is a very stable compound, and not decomposed by red-hot soda lime nor by boiling chromic acid solution. It is not produced by heating acetophenone with alcoholic ammonia.

Acetophenonine hydrochloride forms small thin plates, and is decomposed by water. Nitro-acetophenonine, $C_{24}H_{16}(NO_2)_3N$ (?) crystallises from hot ether in yellowish needles.

The portion of the original product which is insoluble in acids is *triphenyl-benzene*, $C_6H_3(C_6H_5)_3$, which has been produced by a reaction analogous to that by which mesitylene is obtained from acetone, inasmuch as it is also formed by heating acetophenone with phosphorus pentoxide alone:—

$$3(C_6H_5.CO.CH_3) = 3(C_6H_5.C.CH) + 3H_2O.$$

Triphenylbenzene crystallises from ether in well-defined short prisms, melting at 167°—168°. Oxidising agents attack it but slowly, and with bromine and nitric acid it yields substitution-products.

By heating a mixture of aniline, acetone, and phosphorus pentoxide for two days to 180°, a liquid base, boiling between 200°—220° is formed, probably according to the equation—

$$(CH_3)_2CO + H_2N.C_6H_5 = (CH_3)_2C{=}N.C_6H_5 + H_2O.$$

C. S.

Oxidation of Ketones. By A. Popoff (Deut. Chem. Ges. Ber., vi, 560).

On treating dibenzylketone $(C_6H_5CH_2)_2CO$, with an oxidizing mixture of potassium bichromate and dilute sulphuric acid, benzoic acid and carbonic anhydride are produced, but no phenylacetic acid; this is accounted for by the readiness with which phenylacetic acid is oxidised. With regard to the preparation of the ketone, 150 grams of calcium phenylacetate yielded 45 grams of the crude product, which, after purification, melts at 30°, and boils at 320°—321°.

Propylphenylketone yields by oxidation benzoic acid and propionic acid. The pure ketone is a colourless, aromatic liquid, of density 0·992, at 15°; it boils at 218°—221°, and like dibenylketone, it does not form a crystalline compound with acid sodium sulphite. It was prepared by distilling a mixture of calcium butyrate and benzoate, 200 grams of the former to 166 of the latter, in small portions at a time; this quantity yielded 164 grams of the crude ketone.

C. E. G.

Deoxybenzoïn and Analogous Bodies. By B. Radziszewski (Deut. Chem. Ges. Ber., vi, 489—492).

Having come to the conclusion that deoxybenzoïn is benzoyl-benzyl ketone [or rather benzyl-phenyl ketone, $CO\left\{\begin{matrix}C_6H_5CH_2,\\C_6H_5\end{matrix}\right.$] the author endeavoured to prepare it by distilling a mixture of benzoic acid and calcium phenylacetate. After the distillate had been partially freed from benzophenone by distillation, it was evaporated, when crystals of deoxybenzoïn separated.

The author considers it probable that means will be found for effecting the conversion of dibenzyl into deoxybenzoin or benzile, or perhaps the latter may be obtained by the action of water on tetrabromotolane. Deoxybenzoïn and its congeners should then be represented as follows, benzile being regarded as diphenyl-glyoxal and deoxybenzoïn (benzyl-phenyl ketone) being at the same time a ketone and a pseudo-alcohol:—

$$\begin{array}{cccc}
C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5 \\
| & | & | & | \\
CH(OH) & CH(OH) & CH_2 & CO \\
| & | & | & | \\
CO & CH(OH) & CO & CO \\
| & | & | & | \\
C_6H_5 & C_6H_5 & C_6H_5 & C_6H_5. \\
\text{Benzoïn.} & \text{Hydrobenzoïn.} & \text{Deoxybenzoïn.} & \text{Benzile.}
\end{array}$$

The author considers it probable that the oily body which Jena obtained by the action of phosphoric anhydride on benzilic acid is not impure benzile, but an isomeride of this substance, which bears the same relation to benzilic acid and benzile that glycollide bears to glycollic acid and glyoxal.

T. B.

On Optically Inactive Camphoric Acid. By F. WREDEN (Deut. Chem. Ges. Ber., vi, 565).

WITH regard to Jungfleisch's researches on inactive camphoric acid, (*ibid.*, vi, 268), the author points out that mesocamphoric acid, which he believes to be identical with that of Jungfleisch, is readily converted into the inactive modification (paracamphoric acid ?). The author in his paper (*Ann. Chem. Pharm.*, clxiii, 330) says, "I propose to call the new acid mesocamphoric acid, because it is formed under similar circumstances to mesotartaric acid (Dessaignes, Pasteur) and mesaconic acid; and because it may be converted into an optically inactive acid, just like mesotartaric acid into racemic acid (Dessaignes). This change of mesocamphoric acid takes place even on crystallising it out of water or dilute alcohol, and completely on long-continued boiling with very dilute hydrochloric acid."

C. E. G.

Preparation of Mandelic Acid. By OTTO MÜLLER (Arch. Pharm. [3], ii, 385, 389).

MANDELIC acid was discovered in 1852, by Winkler, in the emulsion of bitter almonds, and was afterwards prepared by him from benzoic aldehyde (oil of bitter almonds) by evaporating it with hydrocyanic and hydrochloric acids. Its formula was, however, not elucidated, till Wislicenus formed an analogous substance, ethylidene-lactic acid from acetic aldehyde, hydrocyanic and hydrochloric acids, and proved mandelic acid to be phenylglycollic acid. As benzoic aldehyde does not easily mix with aqueous solutions of hydrochloric or hydrocyanic acid, the author proposed to prepare it from the sodium sulphite addition-product of benzoic aldehyde, by fusion with potassium cyanide, and subsequent treatment with hydrochloric acid. The following reactions took place, as was expected:—

$$C_6H_5CHO + SO_2\left\{\begin{matrix}ONa\\OH\end{matrix}\right. = C_6H_5CH\left\{\begin{matrix}OH\\O.SO_2ONa.\end{matrix}\right.$$

$$C_6H_5CH\left\{\begin{matrix}OH\\O.SO_2ONa\end{matrix}\right. + KCN = SO_2\left\{\begin{matrix}OK\\ONa\end{matrix}\right. + C_6H_5CH\left\{\begin{matrix}OH\\CN.\end{matrix}\right.$$

$$C_6H_5CH\left\{\begin{matrix}OH\\CN\end{matrix}\right. + HCl + 2H_2O = NH_4Cl + C_6H_5CH\left\{\begin{matrix}OH\\COOH.\end{matrix}\right.$$

The melting point of the acid, after purification by crystallisation, was found to be 115°.

W. R.

A New Acid from Aloes. By P. WESELSKY (Ann. Chem. Pharm., clxvii, 65—73).

THIS acid, which the author calls *alorcinic acid*, has already been described (see this Journal [2], x, 489). The present paper gives a few additional details.

The melting point of the acid dried in air is 97°, *in vacuo* over sulphuric acid, 115°. The anhydride melts at 138°.

The *barium salt* crystallises in small needles grouped in masses. It dissolves pretty easily in water and in alcohol, but is quite insoluble in ether. At 100° it becomes rose-red, and begins to decompose. It has the formula, $C_9H_9\frac{Ba}{2}O_3 + 3H_2O$.

The *calcium salt* is rather more soluble. It is anhydrous, $C_9H_9\frac{Ca}{2}O_3$.

The *copper salt*, $C_9H_9\frac{Cu}{2}O_3 + 2H_2O$.

The water of crystallisation of the barium and copper salts cannot be removed at a high temperature without partial decomposition of the salt.

The alkaline alorcinates are difficult to obtain pure, in consequence of the tendency of the acid to oxidise in presence of strong bases. Fused with potash, alorcinic acid is converted into orcin and acetic acid. By treatment with acetyl chloride, it yields a crystallisable *monacetyl derivative*, $C_9H_9(C_2H_3O)O_3 + H_2O$. The author therefore represents the constitution of the acid by the formula, $C_6H_2\begin{cases} OH \\ CH_3 \\ CH_3 \\ CO.OH \end{cases}$.

It seems not improbable that alorcinic acid may be the proximate product of the action of fused alkalis upon aloes, the orcin which is always obtained being the result of its further decomposition. If such is the case, it would, no doubt, be possible to obtain alorcinic acid in larger proportion than hitherto (30 grams from 20 lbs. of aloes) by adopting a modification of the process. The author is making some experiments in this direction.

W. A. T.

Dibromo- and Nitrodibromobenzene-sulphonic Acid. By H. HUEBNER and R. D. WILLIAMS (Ann. Chem. Pharm., clxvii, 117—124).

Dibromobenzenesulphonic Acid is formed by dissolving crystallised dibromobenzene in Nordhausen sulphuric acid. It is very soluble in water, less so in alcohol, and still less in ether, and forms silky needles, which after some time change into compact plates, melting with blackening at about 117°.

$(C_6H_3Br_2.SO_3)_2Ca + 4H_2O$ crystallises in long needles, and is very soluble in water. $C_6H_3Br_2.SO_3Ag + 6H_2O$ is also very soluble, and forms transparent needles. $(C_6H_3Br_2.SO_3)_2Pb + 3H_2O$ crystallises

from a saturated solution in thin, long, six-sided prisms which afterwards change into compact rhombic plates; it is less soluble than the other salts. $(C_6H_3Br_2.SO_3)_2Ba + 2H_2O$ forms slender needles; a similar compound is $C_6H_3Br_2.SO_3K + H_2O$. The sodium salt contains $1\frac{1}{2}H_2O$, and forms long and very soluble needles.

On boiling the acid with fuming nitric acid it yields $C_6H_2Br_2(NO_2)SO_3H$ as a viscid mass, which is readily soluble in water. The potassium salt contains $2\frac{1}{2}H_2O$, and forms small needles. $[C_6H_2Br_2(NO_2)SO_3]_2Ba + 2\frac{1}{2}H_2O$ crystallises in needles. $[C_6H_2Br_2(NO_2)SO_3]_2Cu + H_2O$ forms a syrup, drying up to warty crystals.

$[C_6H_2Br_2(NO_2)SO_3]_2Pb + H_2O$ is much less soluble than the other salts, and forms small reddish needles. The very soluble strontium salt crystallises in microscopic needles.

C. S.

Benzylsulphonic Chloride. By H. LIMPRICHT (Deut. Chem. Ges. Ber., vi, 534).

DRY potassium benzylsulphonate was mixed with an equal weight of phosphorus pentachloride, and the reaction finished by gently heating. The product, after being washed with water, was dissolved in ether and the solution allowed to evaporate; the chloride separated in prisms melting at 92°, and decomposing when more strongly heated into sulphur dioxide and benzyl chloride. Concentrated ammonia converts it into $C_6H_5.CH_2.SO_2.NH_2$, crystallising from water in small prisms melting at 105°.

C. S.

The Acid Derivatives of Naphthylamine. By D. TOMMASI (Compt. rend., lxxvi, 1267—1269).

Naphthylacetamide, $\left.\begin{matrix}C_{10}H_7\\H\\C_2H_3O\end{matrix}\right\}N$, which may be regarded as acetamide in which one atom of hydrogen is replaced by the group $C_{10}H_7$, is formed by the action of chloride of acetyl, acetic anhydride, or glacial acetic acid on naphthylamine, the latter reagent being the most convenient. Naphthylacetamide crystallises in white silky needles, which melt at 152° and sublime at 160°. It is only slightly soluble in boiling water, but readily in alcohol and in dilute acids. By the action of nitric acid it yields a mixture of nitro-compounds, which the author has not yet examined.

Naphthylchloracetamide, $\left.\begin{matrix}C_{10}H_7\\H\\C_2H_2ClO\end{matrix}\right\}N$, prepared by the action of chloride of chloracetyl on naphthylamine, crystallises in colourless silky needles, which melt at 161°, and are soluble in alcohol and in acetic acid.

C. E. G.

Phenolcyanine. By T. L. Phipson (Compt. rend., lxxvi, 1417).

Phenol dissolved in alcoholic ammonia and exposed to the air for many weeks, furnishes a deep-blue resinous substance, which in the dry state has a coppery lustre like that of indigo.

It melts easily and may be partly volatilised in purple vapours. It is soluble in alcohol, ether, and benzene, also in concentrated sulphuric acid. Nitric acid decomposes it, forming a nitro-derivative quite different from picric acid.

Phenolcyanine is very slightly soluble in pure water, but dissolves in alcohol diluted with aqueous ammonia. These solutions are deep blue by daylight. Acids redden them, the blue colour being restored by alkalis.

The solutions of phenolcyanine are completely decolorised by nascent hydrogen developed from zinc and an acid, but not by a mixture of ferrous sulphate and lime.

The author's analyses of this body have not been very satisfactory, but he believes it to be represented by the formula C_6H_3NO, and to have some relation to orcein and to indigo-blue.

W. A. T.

Oxidation-products of some of the Alkaloïds.
By H. Hlasiwetz (Ann. Chem. Pharm., clxvii, 88—89).

Professor Hlasiwetz in a communication to the Vienna Academie d. Wissenschaften, states that Dr. Weidel has succeeded in obtaining, by oxidation of cinchonine, two well-characterised nitrogenous products. One of these is a well-crystallised acid, from which the nitrogen is removed in the form of ammonia on treatment with nascent hydrogen, a crystalline tribasic acid being produced resembling the plant-acids in general character. The second product is also crystalline, but its nature has not yet been definitely ascertained; it appears, however, that cinchonine, $C_{20}H_{24}N_2O$, is composed of a C_{11} and a C_9 group, and that the acid is derived from the former, whilst the second product is a derivative of the latter.

It is proposed to extend this method of examination to the alkaloïds generally.

H. E. A.

Removal of Nitrogen from Alkaloïds. By J. O. Bocke (Deut. Chem. Ges. Ber., vi, 488—489).

In consequence of the recent notice on this subject by Hlasiwetz, the author announces that when quinine is distilled with zinc and zinc-sodium, a distillate is obtained which is free from nitrogen, and possesses an odour like that of cumin oil, sodium cyanide being found in the residue. Cinchonine gave similar results.

Chloroform is a good menstruum for the crystallisation of quinine.

T. B.

Physiological Chemistry.

On the Importance of Common Salt and the Behaviour of Potassium Salts in the Human Body. By G. BUNGE (Zeitschrift für Biologie, ix, 104—143).

THE author investigates the question whether the common salt taken in organic food suffices for the maintenance of the normal quantities of sodium and chlorine in the human body, or whether we are directed by any indications to add to it common salt derived from the inorganic world. He calls attention to the fact that, whilst herbivorous animals take salt together with their organic food, carnivorous animals show reluctance to salted food of any sort; a fact especially remarkable, since the quantity of common salt taken by herbivores in their organic food is not less proportionally than that taken by carnivores: the quantity of potash, however, taken by herbivores is at least double that taken by the carnivores. These two points he investigates by comparing the food of the cat and the ox, and estimating the quantity of potash, soda, and chlorine found in the food. According to the experiments of Bidder, Schmidt, and others, a cat of 3·2 kilograms weight requires 140 grams of flesh for its daily food. Considering that carnivores generally devour whole animals, he takes a number of mice, kills them, and estimates the quantity of potash, soda, and chlorine contained in 140 grams of their bodies. Henneberg and Stohmann found by experiment that an ox weighing 502·5 kilos. required 10 kilos. of clover-hay daily; a second ox, weighing 575·5 kilos., required 27·5 kilos. of red-beet and 7·5 kilos. of oat-straw. Calculating from these data and from tables—given in Wolff's "Ash-analyses"—which show the different quantities of potash, soda, and chlorine contained in different foods for cattle, he arrives at the following results:—

1 kilo. of a carnivore (*e.g.*, a cat) takes daily—

	K_2O.	Na_2O.	Cl.	
When feeding on beef	0·1820	0·0355	0·0310	gram.
" " mice	0·1434	0·0743	0·0652	"

1 kilo. of a herbivore (*e.g.*, an ox)—

When feeding on clover	0·3575	0·0226	0·0433	"
" " beet and oat-straw	0·2923	0·0671	0·3603	"
" " seed grass (?)....	0·3353	0·0934	0·0739	"
" " vetches	0·5523	0·0102	0·0596	"

These results show that the quantity of sodium and chlorine in the food of the herbivore is as great as in that of the carnivore, and the potash twice to four times as much. This excess of potash in the food suggests a hypothesis regarding the reason why herbivores require an

additional quantity of common salt for their proper nutrition, viz., that a decomposition takes place between the potassium salts of the food and the sodium chloride in the blood, whereby potassium chloride is formed, together with new sodium salts, both of which, being in abnormal excess are excreted, and that the deficiency of sodium chloride thus caused has to be repaired by taking that salt directly as food. In order to corroborate this hypothesis, he examines the action of phosphate, carbonate and sulphate of potassium on equivalent quantities of sodium chloride in solution, and finds that in each case a very considerable, though not complete, decomposition takes place.

The author then investigates the action of potassium salts on the sodium chloride in the human body by a series of experiments made on himself in the following manner:—

Expt. I. The experiment lasted 8 days.

Food taken daily: 600 grams of beef, 300 grams of bread, 100 grams of butter, 100 grams of sugar, 2 grams of pure sodium chloride, and 3 litres of distilled water.

The beef was finely minced, well mixed, and then frozen. In this way it was kept fresh whilst a uniform composition was maintained in each daily ration.

He takes every care to have the same quantity of potash, soda, and chlorine in each daily ration of food: these quantities are shown in the annexed table.

TABLE I.

				K_2O.	Na_2O	Na equivalent of the Cl.	Cl.	P_2O_5.	SO_3.		
Taken in the daily food.	In the beef			2·496	0·486	—	0·425	2·748	3·318		
	„ bread......			1·023	0·366	—	0·672	1·533	0·462		
	„ salt			—	1·060	—	1·213	—	—		
	Total........			3·519	1·912	2·019	2 310	4·281	3·780		
	Day of expt.	Date. — July.	c.c. of urine.							Mean temp. of the day.	Weight of body.
										° C.	grams.
Excreted in urine.	1	21	2932	—	—	—	3·802	—	—	14·6	60120
	2	22	3021	2·501	2·695	2·234	2·555	3 085	2·639	17·4	60820
	3	23	2366	2·472	2·088	1 911	2·221	2·903	2·733	16·0	60930
	4	24	2294	2·580	1 846	1·687	1·930	3·016	3·135	19·7	60750
	5	25	1926	13·290	6·921	4 667	5 339	6·379	2·957	21·5	60920
	6	26	1087	4·517	0 889	—	0·764	4·667	3 227	21·1	60110
	7	27	2421	2·702	0·757	—	0 812	3·967	3·132	14·2	60770
	8	28	2567	3·654	1·014	—	1·194	3·729	3·019	11·7	60670

The urine excreted every 24 hours, from 9 a.m. on one day to 9 a.m. on the next, is analysed. At 9 a.m. precisely the bladder is emptied

as completely as possible, and the experiment of the next day is commenced, 1st, by weighing the body, 2nd, by taking the morning's meal. On the 5th day 18·24 grams of potash, as phosphate of potassium, are taken in 3 doses. The results of the experiments are shown in the annexed table :—(Table I.)

The sudden increase of soda and chlorine in the urine on the 5th day can only be attributed to the action of the potassium phosphate. Of the 18·2 grams of K_2O 10·7 have passed through the body and caused the separation of 5·1 Na_2O and 3·4 Cl; *i.e.*, 5·6 grams NaCl and 2·1 grams Na_2O. On the 6th day the soda and chlorine in the urine are far less than normal, since the system is drained of sodium chloride: on the 8th the quantity of sodium chloride begins to increase again.

Expt. II. Diet the same as before, excepting that the bread contains more salt. On the 5th day 18·4 grams of K_2O are taken (as citrate). Of this 12 grams traverse the system on the 5th day, causing the excretion of 3·7 grams of Cl and 4·5 grams of Na_2O (*i.e.*, 6·1 grams of NaCl and 1·3 gram of Na_2O). Calculating from his weight that his blood (which he supposes to be equal to $\frac{1}{13}$th of his body in weight), contains 12·67 grams of NaCl, he infers that very nearly one-half of the sodium chloride contained in his blood has been extracted on the 5th day by the action of the potassium citrate.

TABLE II.

Day of expt.	Date.	c.c. of urine.	Mean temp.	K_2O.	Na_2O.	Na equivalent of the Cl.	Cl.	P_2O_5.	SO_3.
2	11 June	1958	18·4° C.	2·111	3·678	3·126	3·919	2·827	2·893
3	12 "	1910	15·4	2·003	3·155	3·163	3·618	2·168	2·612
4	13 "	2098	7·9	2·013	2·784	2·834	3·212	2·850	2·656
5	14 "	2598	9·9	14·788	7·317	6·033	6·901	1·177	3·014
6	15 "	1786	19·4	4·677	0·486	0·861	0·085	2·372	2·798

He concludes that the separation of the soda from the blood by the action of potash is due to chemical decomposition, and not, as might be supposed, to a mechanical action, since in the latter case the soda would be excreted in the form of phosphate, sulphate, or albuminate, and the tables show that the P_2O_5 is decreased, and the SO_3 scarcely increased, and no traces of albumin could be found in the urine.

TABLE III.

Day of expt.	Date.	c.c. of urine.	KO.	NaO.	Cl.	PO_5.	SO_2.	Mean temp.	Weight of body.
8	July 28	2567	3·654	1·014	1·194	3·729	3·049	11·7°	60670
9	" 29	2461	4·527	9·993	1·011	3·527	3·084	15·7°	60730
10	" 30	2412	1·477	3·614	1·425	3·270	2·915	17·7°	60970

This experiment is continuous with Expt. I (v. Table I) under the same conditions. On the 9th day a quantity of sodium citrate, equivalent to the potassium salts taken in Expts. I and II, was taken in the same manner. The excretion of chlorine is slightly diminished by the action of the sodium salt, a fact which favours the supposition that the changes thus produced in excretion are due to chemical decomposition rather than mechanical action. The excretion of potash is at first increased then decreased, just as the soda is in Expts. I and II. The author regards this experiment as vitiated by the effects of the potassium phosphate taken on the 25th of July (v. Table I).

The fact that in Expt. II the increase in soda is greater than the equivalent increase in chlorine, is not inconsistent with the supposition of a chemical decomposition; for it is possible that the sodium carbonate (formed (1) by the action of the potassium citrate on the sodium chloride; (2) by oxidation from citrate to carbonate) is excreted more rapidly than the potassium chloride; in fact, we see the excretion of potassium chloride increasing on the following day, the quantity of chlorine in the urine being greater than the chlorine-equivalent of the soda, which shows that part of the chlorine must be combined with potash.

It is more difficult to explain the facts of Expt. I by the supposition of a chemical decomposition; for with the 18·24 grams of K_2O, 13·75 of P_2O_5 are taken, of which only 6·5 grams of P_2O_5 (*i.e.*, less than $\frac{1}{2}$) are excreted on the 5th and three following days, whilst 15 grams of K_2O (*i.e.*, for more than half) are excreted during the same time: hence the greater part of the P_2O_5 must be excreted through the intestine. Again, the fact that on the 5th day the increase of soda in the urine equals 5·1 grams, that of the phosphoric acid only 3·1, seems inconsistent with the supposition that the increase of soda is due to the decomposition of the potassium phosphate with the sodium chloride, for then the soda should be excreted as phosphate, and the increase of soda should be to the increase of phosphoric acid in the ratio 31 : 35·5. Probably the reaction is very complicated, and takes place not only in the blood, but also in the stomach (through the medium of the gastric juice) and intestine.

In Expt. I the increased excretion of potash and phosphoric acid continues for 3 days after taking the potash; the author is inclined to think that the potassium phosphate, after absorption into the blood, partly combines with the blood-corpuscles, and is afterwards gradually excreted; and he suggests that it may be one of the special functions of the blood-corpuscles to take up ingredients of the food, such as potassium phosphate, which have been absorbed in abnormal excess in the blood-plasma, so that they cannot be excreted rapidly enough by the kidney, and afterwards to give up these ingredients gradually. The following reasons favour this hypothesis:—

(1.) He finds that by taking citrate and chloride of potassium, the excretion of phosphoric acid is decreased.

(2.) In Expt. I the increase of the phosphoric acid excretion and that of the potash bear no equivalent relation to one another, whilst on the three following days they are very nearly in equivalent proportion.

(3.) In normal blood the potassium salts are contained only in the blood-corpuscles, and chiefly as phosphate.

(4.) Potassium salts, if in the plasma of the blood, act as a powerful poison (0·1 gram of KCl injected into the jugular vein of a dog proved fatal).

TABLE IV.

Day of Experiment.	Date.	c.c. of Urine.	K_2O.	Na_2O.	Cl.	P_2O_5.	SO_3.
2	Oct. 13	2555	2·2995	3·1836	3 1671	2·9182	2·3993
3	„ 14	2552	7·8612	3·5110	5·1035	2 8774	4·1898

On the 3rd day 16 grams of potassium sulphate are taken in doses of 2 grams at intervals of one hour.

The excretion of chlorine is increased 2·2 grams (= 3·6 grams NaCl), that of the soda only 0·33 gram. The reason of this probably is that the soda is excreted as sulphate and carbonate through the intestine, owing to the violent diarrhœa caused by taking the potassium sulphate, a probability supported by the fact that of 7·35 grams of the sulphuric acid taken, only 1·8 appear in the urine.

The author is engaged in experiments on the action of potassium chloride on the body: he finds that it increases the excretion of soda and decreases that of phosphoric acid. He proposes to make his experiments more complete by repeating them and analysing the fæces at the same time, and also to investigate how far the increased excretion of soda and chlorine may be continued by taking potassium salts.

He considers that the results of his experiments, given above, satisfactorily prove that the taking of potassium salts causes an increased excretion of soda and chlorine. How and when the changes take place from which such an increase results, remains to be further investigated. He infers that this action of the potassium salts accounts for the necessity felt by herbivores of taking sodium chloride when they feed on herbs rich in potash; for it may be shown by calculation that on the fifth day of Experiment I, he takes for each kilogram of his body 0·3567 K_2O, 0·0313 Na_2O, and 0·0378 Cl, whilst an ox fed on clover takes for each kilogram of its body 0·3575 K_2O, 0·0226 Na_2O, and 0·0133 Cl (*i.e.*, the same amount of potash and rather less soda). By referring to Wolff's ash-analyses he finds that in the food of carnivores only is the quantity of soda nearly equivalent to that of potash; in the food of omnivores and herbivores the equivalent of potash far outbalances the equivalent of soda. He supposes that herbivores, if unable to obtain chloride of sodium, instinctively supply the deficiency by seeking herbs rich in that salt; and considers that, as a rule, it is necessary to supply chloride of sodium to cattle, and that it is essential to the diet of man, especially to the working classes of Europe who feed largely on vegetables.

C. C.

Results of Feeding with Flesh and Fat. By PETTENKOFER and VOIT (Zeitschr. für Biologie, ix, 1—40).

THE results of experiments made in 1861–63 are here given. A large dog was fed with various proportions of flesh and fat of known composition, and during each diet was placed for one or more days in the respiration apparatus; on these days the whole of the ingesta and egesta were known. By reckoning the nitrogen excreted as showing the quantity of flesh consumed by oxidation, and the difference between the carbon of this flesh and the total carbon in the egesta as expressing the fat oxidised, both the flesh and fat consumed, and by difference the flesh and fat stored up are determined. In the following table the diets and the results obtained are shown in grams per day. The flesh employed contained 22 per cent. of albumin; the fat was anhydrous.

	Nourishment.		Flesh oxidised.	Flesh on or off the body.	Fat oxidised.	Fat on or off the body	Oxygen required by calculation.	Oxygen taken up.
	Flesh.	Fat.						
1	1800	None	1757	+ 43	None	+ 1	—	—
2	400	200	450	− 50	159	+ 41	586	—
3	500	None	566	− 66	47	− 47	330	329
4	500	100	491	+ 9	66	+ 34	323	375
5	500	200	517	− 17	109	+ 91	394	317
6	None	100	159	− 159	94	+ 6	303	262
7	None	350	227	− 227	164	+ 186	522	—
8	800	350	635	+ 165	136	+ 214	584	—
9	1500	None	1518	− 18	None	+ 28	432	466
10	1500	30	1457	+ 43	None	+ 32	480	438
11	1500	60	1501	− 1	21	+ 39	486	503
12	1500	100	1402	+ 98	9	+ 91	479	456
13	1500.	150	1455	+ 45	14	+ 136	493	521

Experiments 1 and 2 were consecutive, so were 3 and 4, 7 and 8, and 10—13. The effect of any diet depends a good deal on the state of the body; a fat, well-fed body will oxidise more albumin and fat than a lean body. The quantity of fat which can be digested and absorbed is very large: with diet No. 8, only 5·2 grams of fat were found in the fæces. As the body becomes fatter, rather less fat is digested. Albumin is far more readily oxidised than fat; the addition of fat to an albuminous diet scarcely diminishes the amount of albumin oxidised. On the other hand, the addition of albumin to a fatty diet diminishes the oxidation of the fat, and greatly increases the amount of fat stored up. If a liberal albuminous diet be long continued, or follow a very low diet, fat is produced from the albumin; but if the same diet follow one rich in fat, the animal for a time loses fat. The authors consider that fat is in all cases produced from the albumin of food, but is generally burnt and not deposited. Fattening is best attained by commencing with a liberal nitrogenous and medium fatty diet, and when the animal frame has sufficiently increased giving more fat and less albumin. The amount of oxygen taken up has no relation to the kind of diet, but rather to its quantity. A maximum consumption of oxygen is not

possible without the circulatory system being largely developed, which implies liberal albuminous diet.

R. W.

Reaction of Milk with Litmus. By A. Vogel (N. Rep. Pharm., xxii, 232—234).

The author has found nearly all the specimens of fresh milk examined by him, either neutral or slightly acid. In only two specimens out of thirty specially examined for the so-called amphoteric reaction, was this found, and in these the alkaline action appears to have been due to traces of free ammonia. He ascribes the acid reaction of fresh milk to the presence of free carbonic acid, since litmus tincture coloured red by fresh milk regains its blue colour on shaking or boiling. No mention is made of the conditions of food, &c., to which the cows were subject.

E. K.

Transformation of Bacteria into Microzymes and of Microzymes into Bacteria, in the Alimentary Canal of Animals. By A. Béchamp and A. Estor (Compt. rend., lxxvi, 1143—1145).

In the stomach of the dog, during digestion, microzymes are found, and various forms of bacteria. Beyond the pylorus, nothing but microzymes are met with till the ileo-cœcal valve is reached. In the large intestine bacteria are abundant. If, however, there be in the small intestine any cause of irritation, as for example a tapeworm, microzymes are immediately developed into bacteria.

T. S.

Chemistry of Vegetable Physiology and Agriculture.

Action of Atmospheric Nitrogen in Vegetation. By P. P. Dehérain (Compt. rend., lxxvi, 1390—1394).

The author has shown (this Journal, 1872, 164), that a mixture of glucose and an alkali heated in air, absorbs not only oxygen but also nitrogen. Glucose and solution of ammonia heated with a confined portion of air in a water-bath, absorbed the whole (9·5 c.c.) of the oxygen, and 17 c.c. of nitrogen; if the absorption had been due to the formation of nitric acid, much less nitrogen would have been removed. No cyanides were produced. When a current of air was passed through a slightly warmed solution of 10 grams of glucose and 40 grams of caustic soda, ·015 gram of nitrogen was absorbed; when nitrogen gas was substituted for air, ·069 gram was absorbed. In these latter experiments the nitrogen was determined by combustion after evaporation, and clearly, therefore, did not exist as ammonia. In experiments made at the ordinary temperature in a eudiometer, negative results were generally obtained when atmospheric air was employed, except in cases in which all the oxygen was taken up; but when nitrogen gas was

employed, absorption generally took place, the mixture of glucose and soda being most active; small absorptions of nitrogen were also obtained from moist sawdust, with or without slaked lime.

R. W.

On the Respiration of Land Plants. By J. Boehm (Deut. Chem. Ges. Ber., vi, 550).

The author found that the volume of oxygen given out by green leaves of land plants immersed in a mixture of carbonic acid and hydrogen, was always greater than the volume of carbonic acid which disappeared.

To discover the reason of this, the air contained in the tissues of living plants must be examined. For this purpose the leaves, &c., were enclosed in a glass tube filled with mercury, and the quantity of gas given out was found to be enormous, and to consist almost entirely of carbonic acid. The mercury was proved to have no influence in the process. The explanation given is that plants in a medium free from oxygen find the necessary material for the performance of their life-processes by internal combustion.

Green leaves of land plants exposed to sunlight in an atmosphere of hydrogen produce only a slight increase in the volume of the gas, and this increase is partly due to oxygen given off. If the leaves are kept three or four hours in hydrogen at a temperature of about 20° in the dark, and then exposed to sunlight, oxygen is given off, but if kept for more than twelve to fifteen hours in the dark, under the same conditions, they lose the property of decomposing carbonic acid when exposed to sunlight, and give off the last-named gas instead of oxygen. Leaves of the *Juglans* kept in atmospheric air in sunlight, at a temperature of 30°, produced no change in the composition of the air, but if the temperature was raised to 40°, or lowered to 6°—10°, more carbonic acid was formed than decomposed. These leaves also acted similarly when placed in an irrespirable atmosphere and exposed to light which had passed through an ammoniacal solution of copper oxide; not only was no carbonic acid decomposed, but some was produced, and the same was the case when gaslight was employed.

The author concludes by stating that pure oxy-hydrogen gas (Knallgas), can only be produced with certainty when the electrolytic apparatus is placed in boiling water.

G. T. A.

Autumnal Colouring of Leaves and Formation of Vegetable Acids. By C. Kraus (N. Rep. Pharm., xxii, 273—296).

The author considers it doubtful if xanthophyll is converted by oxidation into erythrophyll, but regards the red colouring matter of autumnal leaves as due to the presence of pyrocatechin together with organic acids. In red leaves the same xanthophyll grains are seen under the microscope as in yellow leaves, but a red sap is present in addition. Pyrocatechin mixed with citric acid, and exposed to the air, becomes of a beautiful red colour, and after some time ceases to give the reaction with ferric

chloride. Watery extracts of all the autumnal leaves observed gave the reactions of pyrocatechin, but ceased to do so on standing with citric acid in the air. That access of air is necessary to the red colour in plants, is seen in leaves of poplar, &c., injured by insects, or otherwise turning red, also in the young shoots of Mahonia, which are only imperfectly protected by the cuticle, whilst in autumn the cuticle of leaves is so altered that air obtains access to the cells containing the pyrocatechin. It is probable that pyrocatechin is a very generally distributed ingredient of plants. Gorup-Besanez (*Chem. Soc. J.* [2], x, 171) found it in the leaves of *Ampelopsis hederacea*, and it is not unlikely that it has been confounded with, or at all events occurs along with, quercitrin, which it resembles closely in many reactions, and which has been found by various observers in the leaves of the tea-plant, horse-chesnut, and vine. Again, leaves and berries containing much organic acid are generally coloured red. This view is in accordance with the observation of Hoppe-Seyler (*Chem. Soc. J.* [2], ix, 226), that carbohydrates heated in sealed tubes with water, yield pyrocatechin together with formic acid.

The author suggests that chlorophyll decomposes carbonic anhydride into oxygen and carbonic oxide, this latter combining with hydrogen from water to form formic aldehyde, which with water $= CH_2(OH)_2$; this, by polymerisation and abstraction of water, would form a carbohydrate, $C_6H_{12}O_6$, probably on the type of Carius's phenose. This carbohydrate (grape sugar) by elimination of water and oxygen, would form pyrocatechin, the oxygen so set free oxidising other molecules of carbohydrate, to form vegetable acids.

The following formulæ represent the possible simultaneous formation of pyrocatechin and organic acids from grape sugar :—

$$10C_6H_{12}O_6 = 9C_6H_6O_2 + \underset{\text{Oxalic acid.}}{3C_2H_2O_4} + 30H_2O.$$

$$8C_6H_{12}O_6 = 6C_6H_6O_2 + \underset{\text{Malic acid.}}{3C_4H_6O_5} + 21H_2O.$$

$$11C_6H_{12}O_6 = 9C_6H_6O_2 + \underset{\text{Tartaric acid.}}{3C_4H_6O_6} + 30H_2O.$$

$$4C_6H_{12}O_6 = 3C_6H_6O_2 + \underset{\text{Citric acid.}}{C_6H_8O_7} + 11H_2O.$$

E. K.

On the Respiration of Beet-root and the Air inclosed in it.

By A. HEINTZ (Deut. Chem. Ges. Ber., vi, 670—674).

INGENHOUSS observed as early as 1779, that roots, flowers, and fruit continually give off carbon dioxide. To study this slow combustion, the author selected beet-root, which he kept for 30 days under a bell-jar, at a constant temperature of 10°.

	Grams.
Weight of root before the experiment......	4400
Oxygen taken up..........................	25·2
	4425·2
Weight after experiment	4330·5
CO_2 formed	34·3
H_2O „	60·4
	4425·2

This shows that the cane-sugar is oxidised according to the equation:—

$$C_{12}H_{22}O_{11} + 12O_2 = 11H_2O + 12CO_2.$$

The quantity of oxygen calculated from the carbon dioxide being 24·9, while 25·2 were found.

According to these results 1,000 cwt. of beet-root would lose 10 cwt. of sugar in two months.

To examine the gases contained in the root it was ground to a pulp and heated with a little water to 100° for two hours.

In one experiment the composition was found to be in volumes CO_2 = 30 52, O = 0·14, N = 69 34, and in another CO_2 = 35·10, O = 0·56, N = 64·31.

1,000 grams of root gave 130—150 c.c. of gas.

As by the action of heat more carbon dioxide was probably formed than was originally contained in the root, the juice was quickly pressed out and exhausted with Sprengel's air-pump. The experiment lasted five hours and the gases were collected in three portions:—

	(1.)	(2.)	(3.)
CO_2	11·49	41·02	78·90
O	1·53	2·10	0·06
N	86·98	56·88	21·04

C. S.

Examination of Juniper Berries (Juniperus communis).
By E. DONATH (Dingl. polyt. J., ccviii, 300—305).

THE author finds the following substances in juniper berries:—

Water	29·44	Juniperin..........	0·37
Essential oil	0·91	Pectin	0·73
Formic acid........	1·86	Protein substances..	4·45
Acetic acid	0·94	Sugar	29·65
Malic acid	0·21	Cellulose	15·83
Oxalic acid	—	Mineral constituents	2·33
Fat, resembling wax	0 64		
Green resin........	8·46		97·11 per cent.
Hard brown resin ..	1·29		

The wax was extracted with ether treated with water, to remove soluble admixtures, and dissolved in boiling alcohol, which was allowed to stand for some days. The wax deposited was directly weighed. The green resin was obtained by evaporating the alcohol from which the wax had separated out, and appeared to have acid properties and to resemble that obtained from fir.

The substance soluble in water was juniperin; it was obtained on evaporation. It was proved to contain no nitrogen.

The other resin was extracted from the dried berries with alcohol after they had been treated with ether. It is also soluble in alkalis. The pectin was extracted from the dried berries with water and precipitated with alcohol. The formic and acetic acids were separated by distillation with dilute sulphuric acid. Tartaric and citric acids were not present. Malic acid was present, combined with a base.

The essential oil was obtained by distilling the berries with steam.

W. R.

Occurrence of Avic Acid in Guano. By E. Chevreul (Compt. rend., lxxvi, 1376—1382).

The author obtained avic acid from the suint of sheep, and subsequently from the feathers of an albatross (*Compt. rend.*, lxix, 1196, and lxxii, 132); he now recognizes it by its odour in Peruvian guano. The odour is most marked in the residue left by spontaneous evaporation of the watery extract. All the ammonium carbonate of guano can be expelled at a temperature of 90°. The author regards the determination of the proximate principles of manures, and of their behaviour in the soil, and to the plant, as most important.

R. W.

Means of Facilitating the Distribution of Potash in Soil. By C. Treutler (Landw. Versuchs-Stationen, xv, 368—383).

The author continues his previous experiments (*L. Versuchs-Stationen*, xii, 184), on the action of various manures in favouring the distribution of potash. Four pounds of soil were placed in a cylinder, and upon them ½ lb. of soil mixed with a quantity of potassium salt equal to 1 gram of potash, and a known weight of the manure to be tried; the whole column of soil was 29 cm. in height. The soil was next saturated with water, and then 1 litre of water poured on the top; this took 13 hours to drain through, and was poured back twelve times. The potash contained in the litre of drained water was finally determined. Four potassium salts were employed in the two series of experiments. The amount of potash passing through for 100 applied is shown in the following table:—

Substance mixed with potassium salt equal 1 gram K_2O.	Potassium applied as carbonate.	Potassium applied as nitrate.	Potassium applied as sulphate.	Potassium applied as chloride.
Pure water used	1·44	4 91	1·27	3·17
Carbonic acid water used	2·62	3·02	3·79	4·27
Vegetable soil, 250 grams	1·12	2·92	9·93	11·55
Animal manure, 80 grams (mean)	5·40	4·87	4·82	6·82
Bone dust, 50 grams	1·20	2·94	11·02	12·12
Bone dust, 500 grams	29 00	27·20	32·74	25·14
Superphosphate, 20 grams	4·80	7·24	6·24	8·36
Gypsum, 20 grams	4·16	5·98	5·77	6·82
Magnesium sulphate, 5 grams	1·94	9·86	5·87	—
Common salt, 10 grams	—	6·52	2·20	2·80
Sodium nitrate, 20 grams	9·72	7·88	8·20	—
Ammonium carbonate, 20 grams	6·96	6·22	6 81	8·99

R. W.

Analytical Chemistry.

Apparatus for the Quantitative Determination of Carbonic Anhydride in Gases. By B. Wackenroder (Dingl. polyt. J., ccviii, 294—298).

This apparatus is designed to be used in determining the amount of carbonic anhydride in air during various technical operations; thus, in saturating beet-root juice with lime, carbonic anhydride is evolved, which has an influence on the quality of the juice according to the amount in which it is present. Its chief advantages are said to be its transportability and accuracy.

The carbonic anhydride is received in a graduated glass tube which stands in a glass cylinder. The liquid displaced may be water or a solution of common salt. This tube is connected by means of an india-rubber tube provided with a clip, with a wash-bottle half filled with a solution of caustic soda. The tube from the wash-bottle passes through one of the holes of a double-bored cork inserted into one leg of a U-tube, which is graduated on that side. Through the other hole in the cork a tube is passed, provided with a spring clamp. A glass tube, which communicates with a bottle from which water can be forced in by means of an india-rubber ball, is attached to the bend of the U-tube.

The first-mentioned graduated tube is filled several times with the air to be investigated, by means of the india-rubber tube, to expel all atmospheric air. The clamp is then closed, and the india-rubber tube attached to the tube of the wash-bottle. The liquid in the cylinder is brought to the same level with that in the graduated tube by raising or lowering the latter. The amount of gas is then read off. Water is forced into the U-tube (the clamp being kept open) till it reaches the top of the tube at which the figure 0 stands. The clamp is then closed, and the clip on the rubber tube between the wash-bottle and

the graduated tube opened, as well as the clip between the bend of the U-tube and the bottle from which water can be forced in. The gas passes through the caustic soda into the U-tube, where it is again read off. The difference between the original volume and that in the U-tube gives the amount of carbonic anhydride present.

W. R.

Detection of Carbon Disulphide in Mustard Oil. By E. Luck (Zeitschr. Anal. Chem., xi, 410—412).

A small flask is fitted with a cork, through which passes a little test-tube, and also a piece of narrow glass tubing similar in shape to the blowing-tube of a wash-bottle. The small test-tube is also fitted with a cork, through which passes a glass tube, bent downwards and drawn out at its lower end to a point; this end passes through a cork into another test-tube. Water is placed in the flask, and the oil to be tested in the small test-tube. At the temperature of boiling water any carbon disulphide distils over into the small receiver, to which a drop of water has been previously added. On absorbing this water by means of blotting paper, adding ½—1 c.c. of a solution of caustic potash in absolute alcohol, acidulating after a little time with a drop of acetic acid, and adding a drop of copper sulphate solution, a lemon-coloured precipitate (cuprous xanthogenate) is produced. If the quantity of carbon dioxide is very small, only a few oily drops form in the tube connecting the two pieces of the apparatus. These must be washed into the receiving tube with caustic potash in alcohol, and the solution tested as above.

M. M. P. M.

Estimation of the Hardness of Spring Waters. By F. Mohr (N. Repert. Pharm., xxii, 164).

The author criticises a recent review of Wagner's on Clarke's process. He agrees with Wagner that the estimation by means of cochineal tincture and standard hydrochloric acid is preferable to the soap test, but claims priority as to the suggestion of this method. When no magnesia is present, the total lime salts present are conveniently formed by precipitation with ammonia oxalate and titration of the precipitate with permanganate solution. The cochineal test of course indicates sodium and magnesium carbonates as well as calcium carbonate, and does not show the amount of calcium sulphate, nitrate, or chloride.

C. R. A. W.

Estimation of Nitric Acid in Well Waters by means of Indigo. By F. Fischer (J. pr. Chem. [2], vii, 57).

The author refers to the results obtained by Marx, Goppelsröder, Trommsdorff, Scheurer-Kestner, Reichardt, and Bemmelen, in connection with this process, and states, as the results of his own experience, that whilst correct results can be thus obtained with pure

solutions of nitrates, values less than the true ones are apt to be obtained in presence of organic matter, or if too little sulphuric acid be added. Pure acid and pure indigo-carmine must be used.

C. R. A. W.

Note on the Nessler Test. By J. A. WANKLYN (Chemical News, xxviii, 13).

THE rapidity with which the Nessler test develops the full colour with an ammonia solution depends to a great extent upon whether a sufficient quantity of corrosive sublimate has been added to the reagent.

M. J. S.

On the Flame-test for Boric Acid. By BIDAUD (Compt. rend., lxxvi, 489—491).

THE flame of a Bunsen burner, directed upon a crystal of boric acid placed on a piece of porcelain, immediately acquires a splendid green colour. It is not necessary that the crystal should be enveloped by the flame, mere contact with the outer edge being sufficient. The author has made a number of experiments, all showing the sensitiveness of this test.

A centigram of boric acid placed on a piece of porcelain coloured a flame held from a millimeter to a centimeter distant from the porcelain for 25 minutes, the colour being quite distinct in a slightly dark place. Under the same circumstances borax showed only the colour due to sodium, but on addition of a drop of sulphuric acid the green colour at once appeared.

One gram of a solution containing $\frac{1}{2000}$th of boric acid was gently heated in a capsule. A gas flame plunged into the vapours evolved was immediately coloured green. On placing the flame alternately beneath the capsule and in the vapours, the colour remained visible for some time, becoming more distinct as the concentration advanced. The colour was visible also on treating in the same way 5 c.c. of a solution containing $\frac{1}{7000}$th of borax to which a little sulphuric acid was added.

Various salts (calcium sulphate, sodium carbonate, ferroso-ferric sulphate, &c.), added to the solution of boric acid, did not interfere with the reaction. The green colour was more or less persistent, but always distinct in the dark.

J. B.

New Method of Assaying Lead Ores. By A. MASCAZZINI (Dingl. polyt. J., ccvii, 46—48).

THE method is based upon the conversion of the lead into sulphate by heating with ammonium sulphate. The author gives the preference to this salt over heated air, acids, hypochlorites, mercuric oxide, or fusion with nitre or ammonium nitrate. Lead ores which are all but free from other metals may be reduced directly by means of nascent hydrogen (the zinc should be finely powdered), and subsequent fusion

into a button of lead. Ores containing blende or pyrites, however, are first converted into sulphates by means of ammonium sulphate. The quantity of salt required varies with the percentage of metallic sulphides present. Two parts by weight of the dry sulphate usually suffice for the conversion of the richest ores into sulphates. The mixture of ore and ammonium salt is heated in a porcelain crucible covered with a small inverted dish. As soon as the boiling up has ceased, the temperature can be increased to strong red heat, without risk of losing any substance from spirting, till the ferric and cupric sulphates undergo decomposition. The mass when cold is readily dissolved out with hot water acidulated with a little sulphuric and hydrochloric acids. The latter prevents the silver from going into solution, especially if the liquid be diluted and allowed to stand for some time. The insoluble portion, consisting of lead sulphate and silver chloride, is removed by decantation and filtration, and is well washed with hot water, dried, removed to a flask, and treated with powdered zinc and hydrochloric acid as long as any reduction takes place. Two parts by weight of zinc are generally sufficient to reduce one part of pure galena, provided both the metallic zinc and lead sulphate be in the state of a fine powder and intimately mixed. Since even the best kinds of zinc contain a little lead, it is necessary to determine the amount of lead so present, and to make allowance for it. The spongy mass of reduced metals is washed with water freed from air, or with water acidulated with a little dilute sulphuric acid; it is next transferred to a flat basin and pressed with a flattened out glass rod, and thoroughly washed. The mass is then introduced into a crucible, dried at a gentle heat, and mixed with $1\frac{1}{2}$ to twice its weight of a reducing flux, covered with a thin layer of the same, or a little dry sodium chloride, and fused by raising the temperature gradually to red heat.

A flux proposed by Plattner, consisting of—

13	parts	by weight of	potassium carbonate
10	,,	,,	dry sodium carbonate
5	,,	,,	fused borax, and
5	,,	,,	dried starch

effects the fusion readily, and yields a clean metallic button.

The same process is applicable to the analysis of white lead, minium, and litharge, of lead ores containing gold and silver, and by somewhat modifying the fluxes, also to the estimation of antimony, tin, and copper. Should the gold or silver ores be deficient in lead, a quantity of litharge or lead salt is added, sufficient to yield a proper regulus.

W. V.

Estimation of Lead Sulphate in Commercial Lead Chromate.
By E. DUVILLIER (Compt. rend., lxxvi, 1352).

ONE part of the chromate is reduced with 2—3 parts of nitric acid, sp. gr. 1·42, 1—2 parts of water, and a fourth part of alcohol. Water is then added and the whole boiled, when the sulphate alone is left insoluble.

B. J. G.

Detection of Arsenical Colours on Paper or Paperhangings. By H. Hager (Dingl. polyt. J., ccvii, 511).

A piece of the paper or paperhanging is moistened with a concentrated solution of sodium nitrate in a mixture of equal volumes of spirits of wine and water, and allowed to dry.

The dried piece of paper is then burnt on a flat porcelain plate, and usually smoulders without flame. The ashes are treated with water, to which are added a few drops of potash-solution to strongly alkaline reaction, and the liquid is boiled and filtered. The filtrate acidified with sulphuric acid is treated with potassium permanganate so long as decoloration takes place on warming, a slight excess of the permanganate being finally added, leaving a faint red tint. The solution, if turbid, is filtered. After cooling and addition of more dilute sulphuric acid, a piece of pure zinc is introduced into the solution contained in a small flask fitted with a doubly perforated cork. In one perforation is fixed a piece of parchment dotted with silver nitrate solution, in the other a piece dotted with lead acetate. If arsenic be present, the silver paper is soon blackened. The lead paper serves as a check to show the absence of hydrogen sulphide. If the blackening does not occur, or if a slight blackening only, accompanied with a browning of the lead paper, ensues after some time, no arsenic is present.

W. S.

Organic Elementary Analysis. By J. Löwe (Zeitschr. Anal. Chem., xi, 403—408).

The author draws out the combustion-tube to a somewhat narrow point, and fits this by means of a caoutchouc stopper into the bulb of the calcium chloride apparatus. This apparatus consists of a U-shaped tube, the inner edges of the ends of which are very slightly touched with grease (to prevent the calcium chloride caking together when moist); one end of this tube carries a cork, through which passes a small upright glass tube which again is connected (by caoutchouc) with a small bulb-tube; this latter also contains calcium chloride, and it is found that almost all the water is condensed in it.

The author prefers caoutchouc stoppers to ground-glass stoppers for many reasons. He covers these stoppers with a mixture of 1 part gelatin dissolved in 4 parts of water. The caustic potash he prepares by dissolving 1 part stick potash in 1 part water. The small tube attached to the carbon dioxide bulb he fills with glacial phosphoric acid.

To the end of the combustion-tube, where the oxygen enters, the author adapts a glass tube passing through a cork into a small hard glass test-tube, into which the tube through which the oxygen enters, also passes. This latter tube passing to the bottom of the test-tube dips into a small quantity of mercury, whereby any backward diffusion of carbon dioxide is prevented.

M. M. P. M.

Estimation of Paraffin in Stearin Candles. By E. DONATH (Dingl. polyt. J., ccviii, 305).

HOCH gives a method of estimating paraffin in stearin candles, by treating them with not very concentrated caustic soda, precipitating the soap with common salt, which carries down the paraffin, and washing on a filter with cold water, or very dilute alcohol. The soap is washed through, while the paraffin remains. The author found this method extremely difficult to carry out. He proposes to treat about 6 grams of the stearin with 200—300 c.c. of potash-solution of 1·15 sp. gr. The soap is precipitated with calcium chloride. The precipitate is washed with hot water; the paraffin, precipitated with the lime-soap, is not washed through. The mass is then dried at 100° and powdered, and the paraffin extracted by Zulowsky's method with petroleum ether; the extract is evaporated to dryness and weighed. The paraffin, determined in prepared mixtures, agreed to within 0·3 per cent.

W. R.

Adulteration of Essential Oils with Turpentine, and its Detection by means of Alcohol. By G. DRAGENDORFF (N. Report. Pharm., xxii, 1—28).

ABOUT 22 years ago Zeller proposed to detect the admixture of oil of turpentine with other essential oils by the addition of alcohol, the slight solubility of turpentine giving rise to a turbidity in the mixture. A similar proposal has since been made by Hoppe, and this method has subsequently been studied by other investigators, who find that it is only adapted for the detection of turpentine when that substance is present in considerable proportion. This want of delicacy arose from the employment of alcohol in an undiluted state; for when the oil to be examined is miscible in all proportions with absolute alcohol, it forms with this fluid a mixture capable of dissolving a very considerable proportion of oil of turpentine. If, however, the alcohol be diluted until 2—4 volumes of it are required to dissolve 1 volume of the oil, it will be found that the presence of a small quantity of turpentine is indicated by the decreased solubility of the adulterated oil in the diluted alcohol.

To determine the solubility of an oil in alcohol, 2 c.c. of it are placed in a stoppered bottle, and the alcohol is gradually added from a burette, the mixture being well shaken after each addition. The termination of the experiment is known by the liquid becoming clear. A suspected sample being now similarly treated, it will be found that if turpentine be present, a larger proportion of alcohol will be required.

A compendious table is given, showing the solubility of oil of turpentine from different sources in alcohol of various degrees of concentration, the solubility of this oil being found to decrease rapidly as the alcohol becomes weaker.

In testing essential oils for turpentine by means of alcohol, it must be borne in mind that some other oils, such as those of juniper, savin, eucalyptus, and copaiba are but slightly soluble in dilute alcohol; and

consequently may, when mixed with other oils, give rise to appearances similar to those produced by oil of turpentine. Moreover in some cases changes take place in oils which have been kept for a long time, and these must be considered in applying the alcohol test for turpentine. Occasionally also essential oils are adulterated with alcohol; this the author detects by the use of Geisler's vaporimeter.

For the details concerning each individual oil the original paper must be consulted.

T. B.

Discrimination of Pressed and Distilled Oil of Lemons.

By Schack (Zeitschr. anal. Chem., xi, 464).

The ordinary pressed oil makes a puffing noise with iodine; the distilled oil gives no such reaction.

R. W.

Estimation of Alcohol in Commercial Chloroform.

By A. C. Oudemans, jun. (Zeitschr. Anal. Chem., xi, 409—412).

10—15 grams of the chloroform to be tested is placed in a glass flask, excess of dry pure cinchonine is added, and the flask left for an hour on a water-bath at 17° C. with constant shaking. The liquid is then filtered, and 5 c.c. of the filtrate are transferred to a small basin, evaporated to dryness on the water-bath, and the residue is weighed.

The following table shows the amount of residue obtained with varying amounts of alcohol:—

With chloroform containing alcohol.	Residue left by 5 c.c. Milligrams.	Difference.
0 per cent.	21	—
1 „	67	46
2 „	111	44
3 „	152	41
4 „	190	38
5 „	226	36
6 „	260	34
7 „	290	30
8 „	318	28
9 „	343	25
10 „	346	23

M. M. P. M.

Estimation of Sugar. By K. H. Martens

(Deut. Chem. Ges. Ber., vi, 440).

To an excess of a boiling alkaline solution of mercury cyanide. the glucose-containing liquor is added; after cooling the whole is diluted to a known volume and an aliquot part titrated by standard solution of silver nitrate; the potassium cyanide present in the original mercury

cyanide liquor being also determined and subtracted; the glucose is known from the quantity of potassium cyanide formed. This method gives results comparable with those obtained by Fehling's process.

C. R. A. W.

Estimation of Sugar by Barreswil's Process. By E. Feltz (Compt. rend., lxxvi, 1140).

It was found that when the inverted sugar in a mixture of inverted sugar and crystallisable sugar, is estimated by means of copper solution, the resultant number is always too high, the error being greater as the testing operation is more prolonged. The author considers that the inversion of a portion of the sugar is effected by the action of the caustic soda.

T. B.

Vivien's Process for Estimating the Alkalinity of Juice in the Sugar Factory. (Dingl. polyt. J., ccvii, 148—150).

The use of a standard acid so dilute that it will neutralise an equal volume of a solution containing 0 5 gram of lime in a litre.

C. H. G.

Practical Application of Titration to the Estimation of the Alkalinity of Juice in the Manufacture of Sugar. By Jicinsky (Dingl. polyt. J., ccvii, 407—409).—A *practical* (*i.e.*, very rough) method for the use of uneducated workmen.

Simplification of Scheibler's Apparatus for Estimating the Refining value of Raw Sugar. (Dingl. polyt. J., ccvii, 150).

Valuation of Animal Charcoal. By J. B. Schober (N. Repert. Pharm. xxii, 257—265).

The determination of the relative decolorising powers of various specimens of bone charcoal would obviously afford the best means of deciding comparative values. This paper is another attempt to give a working method for effecting this purpose.

A solution of indigo-carmine (6 grams to a litre) is standardised by a solution of one gram of potassium permanganate in 1,000 c.c. water. One gram of the charcoal under examination is added to 50 c.c. of the indigo-solution contained in a flask, the whole well shaken, boiled, and allowed to stand for 24 hours. The proportion of indigo remaining unabsorbed is then determined by the permanganate in an aliquot part of the liquid filtered from the charcoal.

Some determinations made by this method are quoted and compared with those made by the use of caramel or of sugar-lime.*

C. H. G.

* This, like all other processes hitherto proposed, fails to get over the initial difficulty of reducing the various samples to the same state of division, without doing which, the same specimen will give results differing as much as any two from different sources.—C. H. G.

Determination of the Matter absorbed by Animal Charcoal in Refining Sugar. By R. STAMMER (Dingl. polyt. J., ccviii, 317).

THE charcoal through which thick juice had been filtered, absorbed 1·15 per cent. organic, and 0·046 per cent. mineral matter; that through which thin juice was filtered absorbed 0·54 per cent. organic, and 0·07 per cent. inorganic matter. For the juice of 475 beetroots, one filter or 6,300 pounds of charcoal is required; for thick juice, from the same quantity, four-sevenths of a filter, or 3,600 lbs. charcoal. The charcoal through which thin juice had been filtered, absorbed 34 lb. of organic and 4·4 lbs. per cent. inorganic substances; that through which thick juice had been filtered, 41·5 lbs. of organic and 1·6 lb. inorganic substances.

W. R.

Methods of Analysing Grain. By W. PILLITZ (Zeitschr. anal. Chem., xi, 46—63).

THE author commences with a valuable summary of the methods hitherto employed for the determination of starch and cellulose; these methods give widely differing results. When the starch is dissolved by a solution of malt (Oudemans' method), much nitrogenous matter remains with the cellulose, and is not perfectly removed by treatment with caustic potash; moreover, the latter reagent dissolves cellulose to an appreciable extent. Purified cotton-wool lost 4·54 per cent. when boiled with a 1·25 per cent. solution of potash, and afterwards with dilute acetic acid; and on repeating the treatment, suffered a further loss of 2·6 per cent. When vegetable matter is acted upon in the cold by potassium chlorate and nitric acid (F. Schulze's method), the cellulose obtained is very pure; but, unfortunately, purified cotton-wool lost 3·6 per cent. when treated in this manner. The author determines the vegetable fibre in grain by heating the meal with very dilute sulphuric acid in sealed tubes at 140°—145°; under such treatment cotton-wool lost only ·4 per cent. The author's plan of analysis is as follows:—

8—10 grms. of the meal are exhausted with 1 litre of cold water; this must be done as quickly as possible, and is best effected by means of a Real's press. In this press the meal lies on a filter-bed, and water is forced through it by means of a column 7 feet high. In the watery solution total solid matter, ash, nitrogen, and sugar are determined. The undissolved meal is quickly dried, first in a vacuum, then, after being finely powdered, at 100°. 1—1·2 grm. of the dried mass is then treated with 40 c.c. of very dilute sulphuric acid (3—3·5 c.c. of acid sp. gr. 1·16 diluted to 1 litre), and heated in a sealed tube for eight hours at 140°—145°. The cellulose is then collected on a weighed filter, washed with water, alcohol, and ether, dried, weighed, and its ash deducted: it contains only traces of nitrogen. In the solution sugar is determined by Fehling's method, and the amount found is calculated as starch. The heating in the sealed tube is repeated with 1—1·2 grm. of the original meal; the sugar thus obtained represents starch plus sugar and dextrin; by subtracting the starch and sugar previously determined, dextrin is found. Fat, total nitrogen, and ash are determined in the usual manner.

The following are analyses made by the author's method. The millet, buckwheat, and spelt, were free from their external shells; the other grains were in their ordinary marketable condition.

100 parts dried at 100° contain :—	Prince Albert Wheat.	Browick's Wheat.	Spelt.	Rye.	Millet.	Barley.	Oats.	Maize.	Rice.	Buckwheat.
Cellulose..........	3·07	4·76	3·38	4·22	4·28	8·88	18·98	4·82	·87	2·05
Starch............	73·51	70·17	71·60	65·60	69·20	62·65	53·62	72·27	85·41	77·64
Dextrin...........	2 28	5·27	2·16	5·78	1·29	1·96	1·46	·83	1·27	—
Sugar.............	1·56	1·07	1·23	2·17	·52	2·71	·37	1·59	Trace	—
Extractive matter undetermined..	4·54	·81	3·00	3·50	·52	1·73	1·66	1·65	·12	3·65
Fat...............	2·03	1·79	2·72	2·52	4·79	3·08	4·92	5·03	·90	2·89
Albuminoids insoluble	10·89	12·93	10·77	10·60	16·22	14·28	12·13	9·95	10·01	7·40
Albuminoids soluble	·38	·96	2·63	3·87	1·36	2·05	2·69	2·16	·46	4·67
Ash insoluble......	·69	·61	·60	·24	·64	1·23	2·73	·38	·45	·61
Ash soluble........	1·05	1·63	1·61	1·50	1·18	1·45	1·44	1·32	·51	1·09

R. W.

Detection of Digitalin and Atropine. By H. BRUNNER (Deut. Chem. Ges. Ber., vi, 96—98).

THE detection of digitalin in toxicological researches is very difficult. By employing the method of Stas-Otto, the greater part of this glucoside is obtained from the acid ethereal solution as a resinous body, which in most cases does not give the characteristic red colour with sulphuric acid and bromine-water. The smaller portion which is found in the alkaline-ethereal solution, cannot be distinguished from delphinine and aconitine, because delphinine gives the same reaction with sulphuric acid and bromine, and both alkaloïds yield the same results with the phosphoric acid test as digitalin. The latter compound can, however, easily be detected by Pettenkofer's test.

On adding sulphuric acid to a dilute solution of dried bile containing a trace of digitalin, a splendid red colour is produced as soon as the temperature rises to 70°. One c.c. of a decoction of 0·3 gram of foxglove-leaves in 180 grams of water gave the reaction quite distinctly. 0·03 and 0·05 gram of digitalin were dissolved, each in half a litre of Bavarian beer, and the solutions treated by the method of Stas-Otto; no digitalin could be detected in the residue by means of bromine and sulphuric acid, whilst the least trace of it, after being washed with water, gave an intense colour with Pettenkofer's test. Other glucosides give the same reaction, but this does not prevent its application in a toxicological research, if the physiological effects are also taken in consideration. A similar case is the detection of the picrotoxin by means of Fehling's solution, which is also reduced by many other substances.

The residue obtained from the acid ethereal solution may also contain

lactic acid, tartaric acid, colchicine and traces of atropine and picrotoxin, but these bodies are not coloured by Pettenkofer's test, nor are other alkaloïds affected by it, with the exception of narcotine and others which give a red colour with sulphuric acid alone.

The most characteristic tests of atropine are the dilatation of the pupil and the aromatic smell which is produced by adding this alkaloid and a little water to a hot mixture of sulphuric acid and potassium dichromate or ammonium molybdate. The latter reaction, although very characteristic, requires great skill; but it takes place without fail on placing the atropine on a few crystals of chromic trioxide contained in a porcelain basin, and applying a gentle heat until the trioxide assumes a green colour.

C. S.

Determination of Nitrogen in Albuminoïds.

By J. SEEGEN and J. NOVAK (Pfluger's Archiv., vii, 284).

THE authors give a short summary of Novak's research on the determination of nitrogen in albumin (see this Journal, 1872, p. 512), and notice those made by other observers since the question was first raised by Seegen (this Journal, 1871, p. 943), whether a fixed number might be taken as representing correctly the amount of nitrogen in the flesh used in experiments on nutrition. The authors have examined serum-albumin, casein, blood-fibrin, muscle-syntonin, gluten from wheaten flour, and legumin from linseed-meal. The result of their analyses of these substances shows that a different nitrogen content is found according to the method of analysis employed. The amount of nitrogen obtained in the form of ammonia by combustion with soda-lime is always less than that obtained in the gaseous form by combustion with cupric oxide. The difference between the results of the two methods is not the same for all albuminous substances. It is greatest in the case of albumin, amounting to 3·4—3·5 per cent., or more than 20 per cent. of the entire nitrogen content. It is least in fibrin, being only 0·7—1·1 per cent., or about 10 per cent. of the entire nitrogen content. In the case of muscle, the authors obtained 1·7—2·6 per cent., or about 12—18 per cent. of the entire nitrogen content, less by combustion with soda-lime than with cupric oxide.

Combustion with soda-lime always yields a larger quantity of nitrogen when the substance to be analysed is mixed with a considerable quantity of sugar. The entire quantity of nitrogen in it is not obtained, however, by this process, even when the substance is mixed with 12 or 16 times as much sugar. The true nitrogen content of albuminoids, therefore, cannot be determined in this manner. Moreover, the combustion is rendered very tiresome by the admixture with sugar, for the highest temperature continued for four or five hours is necessary for the complete combustion of 3 grams of sugar. The true nitrogen content of albuminoids can only be determined when the nitrogen is obtained in the gaseous form. The results obtained by all other methods are incorrect and must be discarded.

T. L. B.

Separation of Digesting Ferments. By V. Paschutin (Zeitschr. anal. Chem., xi, 464).

The three ferments furnished by the pancreatic glands can be individually obtained by exhausting the glands with concentrated solutions of various salts. Solutions of Rochelle salt, sodium thiosulphate, and ammonium nitrate remove the ferment acting upon albumin; solution of potassium arsenate removes the ferment acting on starch; potassium antimonate and sodium bicarbonate extract the ferment acting upon fat. The ferments of the peritoneal mucus of the dog can be separated by filtration through earthen cells.

R. W.

Testing of Butter for Adulterations. By Hoorn (Zeitschr. anal. Chem., xi, 334—335).

The author employs a glass tube 2 decimeters long, 2 centimeters in diameter for two-thirds of its length, narrower and divided into tenths of a cub. cent. for the other third, and closed at the narrow end. Into this tube are introduced 10 grams of butter, which is melted by means of warm water; 30 c.c. of light petroleum oil are added, and the tube is shaken vigorously and set aside. In 30—40 minutes the petroleum becomes perfectly clear, and contains all the fatty matters in solution. The other constituents of the butter collect in the narrow part of the tube, and their volume may be easily read off. For more exact determinations the fatty layer is poured off and the residue again treated with a fresh portion of petroleum, the whole being allowed to stand for 2—3 hours. Good butter contains from 10 to 14 p.c., adulterated butter, as much as 40 p.c. of impurities, generally water. After separating the petroleum, the undissolved portion may be tested for flour, potato, starch, &c. The fatty solution is tested by evaporating the petroleum completely, dissolving 1 gram of the residue in 7 c.c. of petroleum-spirit in a well-closed flask, and placing the solution in water at 10—15° C. for some hours. Fats of low melting-point being much more soluble than those of higher melting-point, the butter-fat remains in solution, whilst suet, tallow, and even lard, are deposited, if present to the extent of more than 10 p.c.

J. R.

Testing of Butter for Adulterations. By J. Campbell-Brown (Chemical News, xxviii, 11).

The examination of butter for adulterations is based on—1st. Determination of its melting and solidifying points; 2nd. Its taste and smell both before and after fusion; 3rd. A careful microscopical examination with and without the polariscope, and before and after addition of iodine, acetic acid, &c.; 4th. The loss at 100°, which should not exceed 10 per cent.; 5th. The proportion of casein it contains (3 to 5 per cent.) estimated by extracting with ether and hot water; 6th. The salt present (0·5 to 2 per cent. in fresh, and 8 per cent. in salt butter); 7th. A rough determination of its solubility in ether at 18·3°, and if

necessary, a fractional separation of the various fats it contains, with examination of the amount, taste, smell, fusing, and solidifying points of each fraction. Good butter is soluble in about three parts of ether at 18°.

M. J. S.

Method of Distinguishing Pure Ground Coffee from Coffee Substitutes. By J. MULLER (Dingl. polyt. J., ccviii, 80).

A SAMPLE of coffee, adulterated with roasted corn or the like, especially substances containing starch-flour, is tested as follows:—A small quantity of the powdered coffee is shaken with dilute potash-solution, filtered, and the solution diluted with much water; a little iodine solution is now added, when the starch reaction at once ensues if these adulterants be present.

W. S.

Examination of Kirschwasser. By G. BRIGEL (N. Rept. Pharm., xxii, 297—306).

THE various substances and means used in adulterating and imitating Kirschwasser are given in this paper. No good test is known by which the pure article can be distinguished. The author finds that the blue colour which most specimens give with guaiacum is due to a trace of copper derived from the stills.

E. K.

Technical Chemistry.

What Constitutes Pure Water? By E. REICHARDT (J. pr. Chem. [2], vii, 26—37).

THE author's main object is to enforce the (generally admitted) maxim, that the composition of the pure springs of every neighbourhood should be taken as the standard from which to judge of the contamination of particular wells. In his experience the following is the average amount of the principal solid ingredients in pure waters from specific rock formations; the figures refer to 100,000 parts of water:—

Rock formation.	Solid contents.	Organic matter.	Nitric acid.	Chlorine.	Sulphuric acid.	Magnesia.	Lime.	Hardness.
Granite	2·11	1·57	—	·33	·39	·25	·97	1·27
Clay slate	8·80	trace, to 73	trace, to ·05	trace, to ·25	trace, to 2·4	·65	2·25	3·15
Bunter Sandstein	12·5 to 22 5	1·38	trace, to 98	·42	·88	4·80	7·30	13 96
Muschelkalk......	32·5	·90	·02	·37	1·37	2 90	12 90	16 95
Muschelkalk (dolomitic) ..	11·8	·53	·23	trace	trace, to 3·1	6·50	14 00	23 10
Gypsum	236·5	trace	trace	1·61	110·82	12·25	76·60	92·75

The organic matter was apparently determined with potassium permanganate. Analyses of water from the Elbe are given. The Vienna water-supply commission have condemned all river water as untrustworthy for purity.

R. W.

On the Insalubrity of the Water which supplies Versailles. By P. DUCAISNE (Compt. rend., lxxvi, 10, 69).

On the Production of Ammonia Sulphate from Nitrogenous Waste. By L. L'HOTE (Compt. rend., lxxvi, 1083).

THE refuse of wool, horn, feathers, leather, skin, sponge, &c., containing from 6—15 per cent. of nitrogen is, as a rule, not put to any industrial use. The author proposes to manufacture ammonia sulphate, now largely employed in artificial manure from such waste products, by digestion with a solution of caustic soda in 10 parts of water, either in the cold or at a gentle heat, so as not to liberate ammonia, till the mass has assumed a pasty consistence; it is then mixed with quicklime and distilled, at first at as low a temperature as possible, and finally at a red heat. The vapours are collected in receivers containing sulphuric acid of the lead chambers, and the crude ammonia sulphate may be purified by crystallisation. The residue in the retort consists of a mixture of sodium carbonate and quicklime, and may be transformed into sodium hydrate and calcium carbonate by treatment with water.

W. R.

Remarks on the Observations of M. Mène on the Preparation of Ammonia Sulphate from Nitrogenous Waste. By L. L'HOTE (Compt. rend., lxxvi, 1418).

Amount of Phosphoric Acid in Coal Ashes. By LECHATELIER and L. DURAND-CLAYE (Dingl. polyt. J., ccviii, 64—67).

IT is pointed out that whilst the steel manufacturer is anxiously striving to get rid of phosphorus, and to prevent it entering into the composition of his pig to the amount of more than five to six ten-thousandths when Bessemer steel is to be manufactured, the farmer is daily becoming more alive to the necessity of returning to the earth those bodies which are the mineral elements of vegetable growth and fructification, of which phosphoric acid is so important a member.

In the first volume of Percy's "Metallurgy," several analyses of coal ashes are given, of which the ones showing the lowest and highest percentages of phosphoric acid are of the ashes of Dowlais coal. They contain respectively 0·21 and 3·01 per cent.

The authors procured samples of coal from two French coal basins, which were widely separated both as to geographical position and geological condition. From the first coal field three samples were

taken: firstly, of picked pieces of coal; secondly, of washed small coal; thirdly, of coke from washed coal.

From the second basin five samples were taken.

The ashes of the three samples from the first coal basin contained respectively 1·00, 0·20, and 0·75 per cent. of phosphoric acid, whilst in the ashes of the five samples from the second basin the percentages of phosphoric acid were 1·35, 1·12, 0·74, 1·50, and 1·28. Several other investigations on this subject are quoted and analyses given, showing the apparently universal presence of phosphoric acid in coal-ash, in quantities varying from 3 per cent. at the highest to about 0·20 at the lowest. The percentage of ashes in the eight samples of coal above mentioned are: in the first three respectively, 2·90, 4·91, and 11·91; in the remaining five, 5·30, 6·17, 13·27, 9·71, and 5·80.

The absorbent power of the ashes for soluble and volatile manurial substances, together with the amount of phosphoric acid contained in them, point them out as a very promising means of invigorating enfeebled tracts of ground in many cases.

W. S.

On the Alloys Employed for Gold Coinage. By EUG. PELIGOT (Compt. rend., lxxvi, 1441—1453).

THE author has studied certain alloys containing 58 per cent. of gold with the view of ascertaining their suitability for the production of a gold coinage, possessing the advantage of being worth exactly ten times its weight of French sterling silver (90 per cent. of silver and 10 per cent. of copper).

Copper added to gold in larger proportion than 10 per cent. causes the alloy to be dry and brittle during the working. Zinc, or a mixture of zinc and copper, has a similar effect if the proportion of gold much exceeds 60 per cent., but an alloy of 58 per cent. gold, 5—7 per cent. zinc, and the remainder copper is malleable, and has also the colour of a richer alloy. On increasing the zinc to 10 or 12 per cent. the alloy again becomes brittle. The loss of zinc on fusion is trifling, but charcoal must be introduced into the crucible to prevent oxidation.

Replacing the zinc by 6 per cent. of silver also yields a malleable alloy; with 3 per cent. the malleability is far inferior. Tin, on the contrary, cannot be introduced; the alloy is brittle.

The author does not propose the depreciation of the gold coinage, but simply the addition of base alloy to increase the weight.

M. J. S.

On the Conditions Necessary for the Manufacture of Iron Highly Impregnated with Silicon in Blast-furnaces. By SAMSON JORDAN (Compt. rend., lxxvi, 1086—1088).

THE variety of cast-iron, called technically "glazed pig," contains from $1\frac{1}{2}$—$2\frac{1}{2}$ per cent. of silicon; some indeed is manufactured containing 7—8 per cent. The fractured surface is not crystalline; it is smooth to the touch, and brighter the more silicon is present. With a charge of 1,250 kilograms of ore containing 30 per cent of iron, 1,000

kgrms. of coke, and 600 kgrms. of flux, consisting of silica, 50 per cent., alumina 16, lime 33, and manganous oxide 1 per cent. (the proportion of the oxygen of the silica to that of the bases being as 26—17·6), a casting was obtained which was very liquid and filled the moulds without adhering to the sand; it contained 7·90 per cent. of silicon, 0·72 of phosphorus, and 2·60 of carbon; 2,100 kgrms. of coke were required to produce 1,000 kgrms. of iron. The blast employed was feeble, but extremely hot, and the flux contained a large proportion both of silica and aluminia. As the melting point is high, the blast must be hot, and it must be slow to permit of the reduction of the silica by the carbon and iron. Too much lime must also not be present, else the silica will combine with it. The alumina seems to play the part of an acid in combining with the lime.

W. R.

Mixtures for Signal Fireworks. (Dingl. polyt. J., ccviii, 78.)

The following proportions are given in a patent by E. A. Lamarre of Paris, granted to J. H. Johnson of London, for coloured lights for signals:—

White light	100 parts	potassium chlorate.
	10 ,,	antimony sulphide.
	15 ,,	boiled linseed oil.
Red light	50 ,,	potassium chlorate.
	50 ,,	strontium nitrate.
	5 ,,	wood charcoal,

with as much linseed oil as is required to knead the mass together.

Green light	50 parts	potassium chlorate.
	50 ,,	barium nitrate.
	5 ,,	wood charcoal.

and linseed oil as above.

In the specification the use of linseed-oil is claimed as a speciality in substitution of oil of turpentine or resin.

W. S.

On the Effects of Dynamite. By Roux and Sarrau (Compt. rend., lxxvi, 1089—1092).

According to the manner in which dynamite is inflamed, it is capable of producing two different kinds of explosion. When ignited by the detonation of a percussion-cap, nitroglycerin explodes with a force equal to ten times that of gunpowder. This is called an "explosion of the first order;" but if it be lighted, it may explode with a force equal to twice that of gunpowder, and occasion an "explosion of the second order." The results of a number of experiments, made with the view of ascertaining the relative explosive power of gunpowder and dynamite, led to the latter conclusion. Dynamite simply lighted will not detonate, but may produce an explosion of the second class, the force of which is such that one part of nitroglycerin is equivalent to two of powder. The thicker the resisting medium, the more intense the explosion.

If the dynamite be prepared with quartz-sand, it inflames at once, and the explosion ensues through the whole mass; but if some yielding matter, ochre for example, be employed, the portion near the detonating fuse suffers an explosion of the first class, the remainder one of the second. Neither pressure nor temperature has any influence on these phenomena.

W. R.

A Method of rendering Wood and other Fibrous Substances suitable for Pulp to be used in the Manufacture of Paper. By V. E. Keegau (Dingl. polyt. J., ccviii, 316).

Instead of boiling the wood or other fibrous substance with caustic alkali, the author digests it under a high pressure. Pieces of wood half an inch thick and from six to twelve inches long, are placed in a cylinder of iron which is filled with caustic soda of 20°; the liquid is submitted to a pressure of 50 lbs. on the square inch for half an hour. The wood is then heated, by means of steam, to about 300° F. The products resulting from the action of the caustic soda on the resin of the wood are soluble, and may be washed out by soaking the wood in water. It may then be transferred to the pulp machine. The soda may be used again, as but little resin, &c., is dissolved out.

W. R.

Aniline Black. By C. Lauth (Bull. Soc. Chim. [2], xix, 437—441).

The process of dyeing with aniline black employed by the author consists in first mordanting with peroxide of manganese, and subsequently dipping in a cold and strongly acid solution of aniline. The tint is afterwards improved and intensified by various agents. Bichromate of potassium, the salts of copper, of chromium, and of mercury, and especially a mixture of chlorate of potassium, copper salt, and sal-ammoniac effect this purpose.

This process gives fine permanent blacks, but the mordanting is somewhat troublesome, and the black rubs off a little.

W. A. T.

Aniline Black. By C. F. Brandt (Dingl. polyt. J., ccvii, 70—72).

Dyeing of Feathers. (Dingl. polyt. J., ccviii, 318.)

Dr. Ruinann recommends that the feathers be soaked in a solution of ammonium carbonate or sodium carbonate, to prevent them from breaking or bending. After being dyed, the feathers are to be dried by gently placing them in warm air.

Feathers are dyed black in the following manner. Half a pound of feathers is digested at a temperature of 30° in 50 litres of water, con-

taining in solution 1 lb. ignited sodium carbonate. They are then washed with warm water, digested with ferric nitrate of 70° B., and again washed; then heated nearly to boiling with 2 lbs. of logwood and 2 lbs. of quercitron bark. The feathers are left in this bath till they assume a deep black colour. They are then dipped in an emulsion of oil and potassium carbonate, and dried by swinging them in warm air.

To dye feathers brown, they are treated first with catechu and then with potassium chromate. They may be dyed directly with aniline colours. The tips of feathers are made to resemble bronze by painting them with aniline violet dissolved in alcohol of 90 per cent.

W. R.

Reproduction and Inversion of Negatives.
By P. E. Liesegang (Chem. Centr., 1873, 106).

A piece of plate-glass is suffused with a solution of gum, honey, sugar, glucose. and ammonium bichromate, dried, and insolated under the negative, which should be inverted, and dusted over with powdered black chalk. As only the parts of the film not illuminated take up the chalk powder, a new reproduction of the negatives is obtained, the rights and lefts being exchanged. Gemet and Alker, of Paris, substitute graphite powder for black chalk.

The author prefers chalk powder, as it adheres most easily to the film, and in consequence of its brown colour, intercepts strongly the chemically active rays, when in very thin layers.

The following solution is prepared by Gemet and Alker:—100 c.c. of water, 10 grams gum arabic, 10 grams glucose, 2 grams sugar, ½ gram honey, 20 c.c. of saturated solution of ammonium bichromate. For ingrained stereotypes the solution must be quite fresh. In the summer it keeps for only two days. The solution is poured on a well-polished glass-plate, which is allowed to drain for some minutes, and then dried over a spirit lamp. The dried film is insolated under the negative for two minutes, and in the shade for five to six minutes. It is developed by means of a brush dipped in graphite powder. After the first dusting, the picture, though faint, must resemble a direct positive, *i.e.*, as when held over a piece of black paper. The insolation must not last too long or too short a time.

W. S.

Preparation of Gelatin. By F. Hnuze
(Dingl. polyt. J., ccvii, 506—508).

The ordinary methods for producing clear gelatin from thin skins, sinews, cartilage, and bone, and in which before solution these matters are prepared by treatment with hydrochloric acid and lime, always yield a good and faultless article, but at a high price. The author's object is to discover a method for producing a cheaper gelatin of equal quality.

For the experiments, a very bad brown, in fact almost black glue was chosen, which was obtained as a bye-product in a Berlin neat's foot oil manufactory, its price being six thalers per cwt. Placed in

cold water this substance did not swell out like glue, but dissolved to a thick, slightly sticky, and syrupy liquid. For the preparation of this glue, the feet, after separation from leg-bones and hoofs, were taken, and, with the hair still adhering, submitted to the action of superheated steam in closed vessels. The steam is at three atmospheres' pressure, and the action is continued three hours, the solution being run off after standing about half an hour. The strongly ammoniacal glue-solution, separated from the fat, furnishes, after thickening in the steam-bath, the black glue above mentioned, which when quite dry is a very friable mass. Treatment with sulphurous acid or other mineral acids was found unavailing to bleach it effectually or practically on the large scale.

The author endeavoured to ascertain the cause of the blackening, so as to eliminate this if possible in part or altogether. The presence of sulphur and notable quantities of ammoniacal salts in the glue-solution indicated that the action of the superheated steam had been too strong and too much prolonged, so that both cartilaginous and hairy matters had been brought into solution, and blackening had thus resulted in the rapid decomposition of these matters.

In order to reduce this decomposing action to a minimum, the solution is run off from the digestor every hour, instead of only once in three hours, as was done before. After the fat is skimmed off the surface of the liquid, the latter is submitted to the action of fresh wood charcoal, together with 25 per cent. of animal charcoal, and allowed to stand all night. The solution of gelatin is now evaporated at from 20° to 25°, till it attains the right consistency. Four per cent. by weight in carbon of the gelatin in solution is required for the desired result.

After the purification with carbon, an agreeable odour of broth is diffused on evaporating the solution, which is by no means the case when it is not so purified.

A very good article, of very light colour and of a high degree of elasticity and good quality, is obtained.

W. S.

To purify Tallow and make it generally Useful.

(Dingl. polyt. J., ccvii, 516.)

The fresh tallow is melted in boiling water, and is then pressed while hot through a linen filter; it is then boiled in the water and carefully skimmed, allowed to cool and solidify, and then washed with water. Finally it is carefully freed from moisture by pressure, when it may be melted and run into earthenware vessels, which are covered over with bladder, paper, or well-fitting lids. The filtration through linen must be repeated, if necessary, to remove all foreign matters. Thus prepared, the tallow may be used for certain dishes, for pomade when mixed with pure olive-oil, and for ointment and plaster by addition of white wax. Well covered up, it may be kept for a long time, free from smell and rancidity.

W. S.

To Protect Wood from the Influence of Moisture.

(Dingl. polyt. J., ccvii, 515.)

The wood is coated several times with hot linseed-oil varnish, and after drying, is painted with oil colours. Thus treated, it is extremely weather-proof, and is rendered much more durable than by simply coating with paint. The drying, however, requires a longer time.

W. S.

A Glue which Resists the Action of Water.

(Dingl. polyt. J., ccvii, 428.)

Potassium dichromate unites with gum, glycerin, glue, &c., forming, when exposed to light, a substance insoluble in water. By adding a small quantity of a solution of potassium-dichromate, which has been prepared in the dark to glue, a compound is obtained, possessing the cohesive properties of glue, but totally insoluble both in hot and in cold water.

Sausages containing peas were used in immense quantity by the soldiers in the Franco-German war, but a difficulty was experienced in obtaining gut as an envelope for the sausages; parchment-paper was accordingly employed. It was found that ordinary gum would not answer the purpose of joining together the seam, as it could not resist the influence of water. The glue, above described, has been employed with advantage by Dr. Julius Strude in Hamburg. Three per cent. of bichrome is added to the ordinary glue or gelatin solution. The strips of paper, joined by this glue, are dried quickly and exposed to light till the glue changes to a brownish colour; they are then boiled with water containing 2—3 p.c. of alum till all potassium dichromate is extracted, and then washed in cold water and dried.

W. R.

Paste from Rice Starch.

One hundred and twenty grains of rice starch and twenty grains of gelatin are mixed with two ounces of water, and then heated over the flame of a spirit-lamp with constant stirring. When the milky liquid becomes thick and glassy, the paste is ready. It is kept in a well-closed box, and near an open flask containing spirits of wine. The paste is of excellent quality, and will keep good from eight to fourteen days.

W. S.

Easy Method of Cleaning Silver. By Dr. Elsner

(Dingl. polyt. J., ccviii, 320).

The silver is cleaned in water in which potatoes have previously been boiled. A polish is produced equal to that obtained by using the best powders.

W. R.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XLIII.—*Oenanthylic Acid and Normal Heptyl Alcohol.*

By HARRY GRIMSHAW and CARL SCHORLEMMER, F.R.S.

Oenanthylic acid, $C_7H_{14}O_2$, was discovered in 1841 by Tilley (*Ann. Chem. Pharm.*, xxxix, 160). He obtained it by oxidising castor-oil with nitric acid and distilling the product with water. A similar acid, called *azoleic acid*, had already been found by Laurent in 1837 among the products formed by the action of nitric acid on stearic acid. Tilley thinks that these two acids were probably identical.

Oenanthylic acid was afterwards examined by Bussy, who found that its aldehyde, or *oenanthol*, was produced by the dry distillation of castor-oil. He obtained the acid by oxidising this compound with nitric acid and with chromic acid (*Ann. Chem. Pharm.*, lx, 246). Williamson showed that the same acid is produced by the action of caustic potash on oenanthol (*Ann. Chem. Pharm.*, lxi, 38); and Tilley, who examined oenanthol more carefully than Bussy had done, also prepared it by these different methods (*Phil. Mag.* [3], xxxiii, 81, and *Ann. Chem. Pharm.*, lxvii, 103).

Redtenbacher observed oenanthylic acid among the products obtained by oxidising oleic acid with nitric acid (*Ann. Chem. Pharm.*, lix, 41), and Schneider obtained it by acting with nitric acid on the products of the dry distillation of rape-oil (*Ann. Chem. Pharm.*, lxx, 107). Arzbaecher found that it is also formed when castor-oil is oxidised with potassium dichromate and dilute sulphuric acid.

Tilley describes oenanthylic acid as a colourless limpid liquid, possessing an aromatic odour. After being dried over glacial phosphoric acid, it begins to boil at 148°, but when kept at this temperature for a long time it suddenly blackens and undergoes decomposition. This undoubtedly shows that Tilley's acid was a very impure compound, for a fatty acid containing seven atoms of carbon must boil without decomposition above 200°; moreover, he found 0·7 per cent. too much carbon.

In Strecker's "Lehrbuch" it is said that this acid boils at 212°, and the same boiling point is found in Gmelin's and most other hand-books. On whose authority this number is given we are unable to state; it appears not improbable that it was calculated according to Kopp's law.

Staedeler says (*J. pr. Chem.*, lxxii, 240) that the acid obtained by

the spontaneous oxidation of oenanthol boiled under a pressure of 725·9 mm. at 118°, and not at 112° as generally stated. These numbers are obviously misprints for 218° and 212°, as has already been pointed out in the *Jahresbericht* for 1857.

Landolt, who prepared this acid by Tilley's original method, found that the product began to boil at 208°, and that half of it distilled constantly between 218 5° and 220° under a pressure of 756·5 mm., and left a black residue (*Pogg. Ann*, cxvii, 379).

One of us, by oxidising the alcohols obtained from normal heptane, obtained an acid having the composition of oenanthylic acid, and boiling at 219°—222°. As it appeared probable that this acid might be identical with oenanthylic acid, some of the latter was prepared and found to boil under the same conditions at 219°—221°.* On heating equal quantities of the two acids with water and barium carbonate, and evaporating the two solutions to exactly the same volume, thin iridescent plates appeared on cooling, which grew into large plates and broad needles; both salts are anhydrous. From this it was concluded that the two acids are identical (*Phil. Trans*, clxii, 121).

Since that time Franchimont has obtained by synthesis an acid having the same composition. He converted the hexyl alcohol from Heracleum oil into the nitrile, and decomposed it with caustic potash. The *heptylic acid* thus formed is an oily liquid, boiling under a pressure of 762·7 mm. at 223°—224°, the whole column of the mercury being in the vapour (*Ann. Chem. Pharm.*, clxv, 237).

Franchimont thinks that this acid is most probably identical with that derived from normal heptane, because Zincke and he found that their hexyl alcohol yielded normal caproic acid by oxidation. But it cannot be identical with Tilley's acid, if the latter was a pure compound. He then adds, "This point assumes a different aspect by Schorlemmer's assertion that oenanthylic acid has the same properties (of which, however, only the boiling point is given) as the acid from heptane. But as Schorlemmer describes no other properties, and as seemingly he has not prepared any derivatives besides the barium salts, such a comparison appears very difficult, and in this case at least too venturesome; although it is possible, and even not improbable, that the two acids are identical. By the oxidation of castor-oil with nitric acid a whole series of acids is produced, according to several statements, and it appears to depend on the strength of the nitric acid, as well as on the temperature and duration of the action, which of the acids is obtained in the largest quantity, and therefore the possibility exists (for Tilley found also caproic acid) that a mixture is produced having the observed boiling point (one has only to remember

* These boiling points are not corrected, but were determined at the same time with the same thermometer.

butyro-acetic acid), and then the similarity of the two barium salts is not sufficient reason for declaring the two acids as identical."

Now in the paper referred to it is not stated at all that the oenanthylic acid used for comparison was prepared by oxidising castor-oil with nitric acid. It is a well-known fact that nitric acid is not the best oxidising agent for preparing pure fatty acids, because it readily acts on them and oxidizes them further. It is true that Brazier and Gossleth, who prepared oenanthylic acid in quantity, found that Tilley's original method gave a better yield than any other (*Quart. Journ. Chem. Soc.*, iii, 210, and *Ann. Chem. Pharm.*, lxxv, 249). But as Bussy had already prepared it by oxidising its aldehyde with chromic acid, this method appears to be the only rational one, and for this reason the acid which was compared with that derived from heptane, was obtained by oxidising pure oenanthol with potassium dichromate and dilute sulphuric acid.

Tilley not only analysed his acid, but also prepared the ethyl-ether and a series of salts. But as his acid was very impure, most of the compounds which he describes were also undoubtedly impure substances. None of the other chemists who worked on oenanthylic acid examined any of the derivatives more minutely, and therefore it appeared necessary to undertake a new research on this acid, the results of which we have the honour to lay before the Society.

Preparation of Oenanthylic Acid.—To obtain this acid in quantity, the following method was found to answer best. Castor-oil is subjected to a rapid dry distillation, and the oenanthol purified by fractional distillation. It is not necessary to use a perfectly pure oenanthol; the portion boiling between 150°—160°, containing still some acrolein and other products, may be employed, as the acid obtained from it can easily be purified.*

300 grams of oenanthol are gradually added to a warm solution consisting of 300 grams of potassium dichromate, 450 grams of sulphuric acid, and 900 grams of water. After the action is over, the flask is connected with a reversed condenser, and the liquid boiled for

* On rectifying a large quantity of oenanthol, we found that the boiling point remained for a very long time perfectly constant at 154°, the whole column of the mercury being immersed in the vapour. According to Tilley it boils at 155°, and according to Staedeler at 151°—152°, the latter observation being probably not corrected. The thermometer used for this determination was one of Geissler's new ones, which Zincke has described (*Ann. Chem. Pharm.*, clxi, 91). These thermometers are very short, having as fixed points the boiling point of water and that of naphthalene, which boils constantly at 217°, according to Geissler. The same thermometer was used for determining the boiling points of the acid and its ethyl-ether. After these experiments were finished, the fundamental points were redetermined, and it was found that, under a pressure of 761·7 mm., water boiled at 100·8°, and pure naphthalene at 218°.

some hours. After cooling, the two layers of liquid are separated, and the lower one, containing some oenanthylic acid in solution, is distilled, and the distillate saturated with soda. The upper layer is well shaken with caustic soda, to remove chromic oxide, and the solution of the sodium salt evaporated. On adding sulphuric acid to the concentrated liquid, oenanthylic acid separates out as an oily layer, which was washed with water, and dried over phosphorus pentoxide.

The acid thus obtained contains some acrylic acid, and begins therefore to boil a little above 140°; the boiling point soon rises to 200°, and then more slowly to 230°; at the same time the liquid blackens, and a dark residue is left in the flask. On rectifying the higher-boiling portions, it again leaves a dark residue, and water is formed; the distillates must therefore be dried over phosphorus pentoxide, and the fractional distillation continued, until the acid has a constant boiling point, does not act any longer on phosphorus pentoxide, and volatilises without leaving a residue.

Oenanthylic Acid and Oenanthylates.—Pure oenanthylic acid is a limpid, oily liquid, boiling under a pressure of 763 mm. at 223°—224°. The cold acid has a faint smell, like that of tallow, but on heating it becomes unpleasantly sour and pungent. In a freezing mixture it soon solidifies to plates, or large broad needles. To determine the melting point a quantity of the acid was placed in a wide test-tube of thin glass, and a delicate thermometer, having a correct zero-point, was placed in the centre of the liquid. At −10° the first crystals appeared, and at − 11° the whole was a solid mass. The tube was now removed from the mixture of ice and salt; at −10·5° the crystals began to liquefy, and at −10° every crystal had disappeared. Oenanthylic acid, therefore melts and solidifies at −10·5°.

Franchimont's heptylic acid melts at −8°, but he adds that from repeated experiments it appeared that the melting point was probably 2° lower.

The acid obtained from heptane does not solidify in a freezing mixture. This is, however, no proof against its identity with oenanthylic acid, for it is well known that the melting point of a fatty acid is much lowered by an admixture of other acids. Now the heptane from which the acid was obtained had to be separated by fractional distillation from an isomeride boiling only 7° lower, and from an octane boiling about 17° higher, and therefore certainly contained some of these hydrocarbons: consequently the acid also would contain acids corresponding with the hydrocarbons.

The specific gravity of oenanthylic acid, compared with water at 4°, was found to be—

At	0°	=	0·9345
„	8·5°	=	0 9278
„	16°	=	0 9208
„	29°	=	0·9110

Staedler found it at			24°	=	0·9167
Landolt	„	„	18°	=	0·9179
„	„	„	20°	=	0·9175

The acid from heptane gave the following results:—

At	0°	=	0·9359
„	9°	=	0 9388
„	28°	=	0·9235

Heptylic acid has at 24° the specific gravity, 0·9212.

The analysis of the acid gave the following results:—

0·2426 gave 0 5744 CO_2 and 0·2300 H_2O.

	Calculated.		Found.
C_7	84	64·61	64·57
H_{14}	14	10·77	10·53
O_2	32	24·62	—
	130	100·00	

Ethyl Oenanthylate, $C_7H_{13}(C_2H_5)O_2$, was prepared by mixing equal volumes of oenanthylic acid and absolute alcohol with half a volume of concentrated sulphuric acid, and heating the mixture for some hours on a water-bath. The ether which separated as a light colourless layer was washed with water and very dilute soda-solution, dried over calcium chloride, and finally over some phosphorus pentoxide. After being purified by fractional distillation, it was obtained as a limpid and very refractive liquid, possessing a fragrant, fruity smell, and boiling under a pressure of 763 mm. at 187°—188°, the whole mercurial column being immersed in the vapour.

0 1936 gave 0 4848 CO_2, and 0·1977 H_2O.

	Calculated.		Found.
C_9	108	68·35	68·29
H_{18}	18	11·39	11·34
O_2	32	20·26	—
	158	100·00	

It has at 16° the specific gravity 0 8735, and does not solidify at −20°, whilst Tilley's ether, which was not purified by fractional distillation, solidified in a freezing mixture.

Ethyl heptylate boils at the same temperature, and has at 21° the specific gravity 0·874; it also does not solidify at −18°.

Potassium Oenanthylate was obtained by allowing its aqueous solution to evaporate at the common temperature, as a transparent jelly; Tilley's salt has the same properties.

Sodium Oenanthylate crystallises in slender ramified needles, when a warm solution is cooled down slowly, whilst on cooling a concentrated down quickly, it solidifies to a gelatinous mass, in which, however, under the microscope, distinct needles can be seen.

Sodium heptylate possesses very similar properties.

Barium Oenanthylate, $(C_7H_{13}O_2)_2Ba$, was prepared by boiling the acid with water and pure barium carbonate; it crystallises from a hot concentrated solution in very thin, small plates, and from a more dilute solution it separates first in little iridescent plates, which soon grow into large plates or flat needles. On evaporating the mother-liquor over sulphuric acid, it crystallised in long needles grouped in stars. This salt has already been described and analysed by several observers.

0·1767 gave 0·0877 $BaCO_3$.

	Calculated.	Found.
Ba	34·68 per cent.	34·51

To determine its solubility, an excess of the salt was added to water contained in a stoppered bottle, and the mixture frequently shaken and kept for several weeks in a cellar having a constant temperature. As most oenanthylates form basic salts on evaporating their solution, the barium was determined as carbonate.

10 c.c. of the solution saturated at 12° gave 0·0848 $BaCO_3$. 100 c.c. contain therefore 1·700 grams of barium oenanthylate.

The barium salt of the acid from heptane has very similar properties; its solubility was determined at the same time.

10 c.c. of the solution saturated at 12° gave 0·0885 $BaCO_3$, or 100 c.c. contain 1·774 grams of the dry salt.

Franchimont did not determine the solubility of barium heptylate, which also crystallises in anhydrous thin plates.

Calcium Oenanthylate, $(C_7H_{13}O_2)_2Ca + H_2O$, was prepared by precipitating a solution of the sodium salt with calcium chloride, and crystallising the washed precipitate from boiling water. It forms very thin, flat, fascicular needles, which dry up to a silky mass.

0·2690 lost at 180°, 0·0160 H_2O.
0·2530 of the dried salt gave 0·0490 CaO.

	Calculated.	Found.
H_2O	5·70	5·94
Ca..........	13·42	13·83

The acid from heptane yields a very similar salt, having the same composition.

0·0632 lost at 180°, 0·040 H_2O.
0·0592 of the dried residue gave 0·0108 CaO.

	Found.
H_2O	6·33
Ca	13·03

The solubility of the two salts was determined by leaving an excess of them in contact with water for six weeks, the mixture being kept in a cellar and frequently shaken.

10 c.c. of the solution of calcium oenanthylate saturated at 8·5° gave 0 0170 CaO.

10 c c. of the solution of the salt from heptane at the same temperature, gave 0·0170 CaO.

The two salts possess therefore the same solubility; 100 c.c. of a solution saturated at 8·5° contain 0·9046 grams of the anhydrous salt, or 0·9593 of the crystallised salt.

Calcium heptylate has the same composition, but its solubility has not been determined by Franchimont.

Zinc Oenanthylate, $(C_7H_{13}O_2)_2Zn$, was obtained by adding zinc sulphate to a solution of the sodium salt. The dried precipitate was crystallised from absolute alcohol; on cooling the solution quickly, very small needles are obtained, which, when dry, form silky scales, feeling soft, like powdered talc. When the solution cools down slowly, the salt crystallises in short four-sided prisms. The salt contains neither alcohol nor water, and may be heated without undergoing any change up to 130°, at which temperature it melts, and above this temperature it begins to decompose.

0·1527 of the needles lost at 100° only 0·0009
and the residue left on ignition 0 0380 ZnO.

	Calculated.	Found.
Zn........	20·17	20·10

Franchimont's zinc heptylate crystallises also in short prisms, which, however, contain two molecules of alcohol; the dried salt melts at 131°—132°. As we once obtained our salt in larger prisms, we dried some quickly between filter-paper, and heated a weighed quantity first to 83°, and then to 100°; but no loss of weight took place, showing that it did not contain alcohol.

Lead Oenanthylate, $(C_7H_{13}O_2)_2Pb$, was obtained by adding lead acetate to a solution of the sodium salt, as a heavy precipitate, which is not very freely soluble in boiling water, but may be crystallised from it, and is thus obtained in thin, small, iridescent, rhombic plates, or flat needles grouped in stars

0·2875 of the crystallised salt dried at 125° lost 0·002, and the residue gave 0·1370 PbO.

	Calculated.	Found.
Pb........	44·51	44·23

Lead heptylate is a similar salt; the precipitated compound melts, according to Franchimont, at 79°—80°. We found that our lead salt only softens at this temperature, and becomes perfectly liquid and transparent only at 90°. The crystallised salt begins to soften at 88°, and liquefies completely at 94°—96°; it solidifies again at 75°—76°.

Tilley describes lead oenanthylate as a lemon-yellow powder, insoluble in water; it appears very probable that this salt owes its colour to a nitro-compound which was present in Tilley's acid.

Copper Oenanthylate, $(C_7H_{13}O_2)_2Cu$, falls down as a soft mass, on adding copper sulphate to a solution of the sodium salt, but on standing the precipitate becomes granular. It is quite insoluble in boiling water, but dissolves readily in absolute alcohol, and is obtained by spontaneous evaporation in green silky needles, or short prisms.

0·2055 gave 0·0501 CuO.

	Calculated.	Found.
Cu........	19·75	19·47

The copper salt of the acid from heptane, and copper heptylate, are similar precipitates. The former could not, however, be obtained in crystals, but separated from the alcoholic solution as a liquid, drying up to an amorphous mass. Copper heptylate also is first obtained in drops, which afterwards solidify to groups of short prisms.

We prepared our copper salt several times, but it never separated from an alcoholic solution in the liquid state, the solution yielding distinct crystals to the last drop. Tilley also obtained a copper salt, crystallising in green silky needles.

Silver Oenanthylate, $C_{11}H_{13}O_2Ag$, is a white precipitate, crystallising from boiling water, in which it is but sparingly soluble, in small, woolly needles.

0·2150 gave 0·0981 Ag.

	Calculated.	Found.
Ag........	45·57	45·63

The quantity of the acid from heptane was too small to admit of a more minute study, but as the barium salt and calcium salt have the same composition and solubility as the corresponding oenanthylates, we believe that these two acids are identical.

Heptylic acid also bears the greatest resemblance to oenanthylic acid; only the copper and zinc salts exhibit slight differences. Whether these are essential or not, can only be decided by preparing the salts

under exactly the same conditions, and comparing them directly with each other.

There can be no doubt that oenanthylic acid and heptylic acid are both normal compounds; this, however, does not imply that they are really identical. It is not only possible, but even very probable, that the hexyl alcohol from heracleum-oil, as well as the heptylic acid obtained from it, are optically active, while oenanthylic acid probably does not possess this property.

Normal Primary Heptyl Alcohol, $C_7H_{16}O$.—As by distilling castor-oil any required quantity of oenanthaldehyde may be obtained, this compound appears to be the best starting point for the preparation of the hitherto almost unknown normal heptyl compounds.

Some years ago Bouis and Carlet found that by acting with zinc and acetic acid on oenanthol under pressure, a heptyl acetate is formed, boiling at 181°, and yielding a heptyl alcohol boiling at 165° (*Ann. Chem. Pharm.*, cxxiv, 352).

If these statements be correct, this alcohol cannot be a normal compound, for its boiling point is only 8° higher than that of normal hexyl alcohol. One of us, on repeating these experiments, did not, however, succeed in obtaining a heptyl alcohol, the chief product of the reaction consisting in high-boiling condensation-products of oenanthol (*Ann. Chem. Pharm.*, cxxxvi, 261).

To convert oenanthol into the alcohol, we have therefore made use of the excellent method which Lieben and Rossi have employed so successfully for the reduction of other aldehydes.

Oenanthol was shaken with fifty times its weight of water; and a little more than the required quantity of an amalgam containing 1 per cent. of sodium was gradually added, together with an equivalent quantity of dilute sulphuric acid, care being taken to keep the liquid always slightly acid. As soon as the action was over, the liquid was distilled, and the distillate again treated in the same way with the amalgam. The alcohol floating on the top was then removed, and the portion remaining in the aqueous solution isolated by repeated distillation, the alcohol always coming over with the first portion, from which it was finally separated by adding potassium carbonate. The product was dried over ignited potassium carbonate, and the alcohol separated from another very high-boiling liquid by fractional distillation. To get rid of some oenanthol and water which were still present, the liquid was several times distilled over small pieces of sodium, and then left for several weeks in contact with anhydrous baryta.

Normal heptyl alcohol is a limpid oily liquid, possessing an aromatic odour, and boiling under a pressure of 766 mm. at 175·5°—177·5°, the whole column of mercury being surrounded by the vapour.

0·2800 gave 0·7405 CO_2 and 0·3183 H_2O.

	Calculated.		Found.
C_7	84	72·4	72·13
H_{16}	16	13·8	13·81
O..........	16	13·8	—
	116	100·0	

This alcohol, as well as other normal heptyl compounds, will be fully described in a second communication.

We are now acquainted with the complete series of normal alcohols up to octyl alcohol. The following table shows that the boiling points increase very regularly for each increase of CH_2. The boiling points which are here given were determined either by the whole column of the thermometer being immersed in the vapour, or, if this was not the case, the required corrections were made:—

Table of Normal Alcohols.

	Boiling-point.	Difference.	Observer.
Ethyl alcohol	78·4°	—	Kopp.
Propyl alcohol	97°—98°	19°	Different observers.
Butyl alcohol	116°	18·5°	Lieben and Rossi.
Pentyl alcohol	137°	21°	Lieben and Rossi.
Hexyl alcohol	157°	20°	Franchimont and Zincke.
Heptyl alcohol........	175·5°—177·5°	19·5°	H. G. and C. S.
Octyl alcohol	196 —197°	20	Renesse.
Mean......	..	19·6°	

XLIV.—*On some Oxidation- and Decomposition-products of Morphine Derivatives.*

By E. Ludwig Mayer, of Glasgow, and C. R. A. Wright, D.Sc., Lecturer on Chemistry in St. Mary's Hospital Medical School.

When solution of caustic potash is added to solution of apomorphine hydrochloride, the base is precipitated, and speedily redissolves in excess of the precipitant. The solution thus obtained, colourless at first, very rapidly becomes dirty purple or brown, and finally black, an insoluble amorphous black deposit being simultaneously produced. This change is accompanied by an absorption of oxygen, which is so energetic that the alkaline solution can be used (like pyrogallol solution) for the determination of oxygen. Thus, 17·9 c.c. of air (reduced to 0° and 760 in an absorption-tube) were allowed to stand in contact

with 0·1 gram of apomorphine hydrochloride dissolved in caustic potash:—

Oxygen absorbed in 2 hours, 10·7 per cent.
„ „ 16 „ 20·9 „

and in another experiment, 0·2 gram of apomorphine hydrochloride absorbed in five days from 82·9 c.c. of air (at 0° and 760)

20·4 per cent.

Average percentage in air (Bunsen) 20·9 „

If the oxidised solution thus obtained be acidified with hydrochloric acid and agitated with ether, the ether dissolves out a substance which communicates to the ethereal liquid a magnificent red-purple tint resembling that of permanganate solutions. The production of this colour serves indeed as a good qualitative test for apomorphine, a moderately deep tinge being given to a small quantity of ether by a minute fraction of a milligram of that substance, when dissolved in caustic potash, exposed to the air for an hour, acidified, and agitated with ether.

By evaporation of the ether, an indigo blue-black deposit is left, exhibiting faint traces of crystalline structure. This deposit mainly consists of a colouring matter, which is soluble in alcohol, chloroform, benzene, carbon disulphide, ether, alkaline liquids, and water containing much ammoniacal salts, although insoluble in pure water or dilute acids. The tint communicated to a given bulk of solvent by a given weight of material varies with each solvent, being cerulean blue with solutions of ammoniacal salts, grass-green with dilute sodium carbonate, and of different shades varying from blue to violet and almost crimson with the other solvents above named. The absorption-spectra of solutions of equal strengths but with different solvents are now under investigation by Dr. Gladstone.

To obtain this colouring matter in as pure a state as possible, the crude ethereal solutions were agitated with sodium carbonate solution, and the bright green aqueous liquid thus obtained was acidified with hydrochloric acid. Indigo-blue flakes were thus precipitated, which dissolve, all but traces, in ether. This process was repeated several times, the product finally obtained being wholly soluble in ether, the solubility, however, not being very great, a litre of ether taking up only a few decigrams of substance. Neither the precipitated flakes nor the residue left on evaporation of the solution in ether, chloroform, &c., exhibited any very well defined crystals, although traces of crystalline structure were usually visible, one specimen being distinctly crystalline. The following numbers were obtained:—

A. Precipitated flakes prepared as above—

0·2430 gram gave 0·653 CO_2 and 0·118 H_2O.
0·2880 „ 0·0885 Pt (burnt with soda-lime).

B. Another specimen of flakes from another preparation—
0·2125 gram gave 0·5715 CO_2 and 0·1040 H_2O.

C. Residue left on evaporating ethereal solution of purified flakes—
0·2390 gram gave 0·6470 CO_2 and 0·1170 H_2O.
0·2470 „ 0·0730 Pt.

	Calculated.		Found.		
			A.	B.	C.
C_{40}	480	73·40	73·27	73·35	73·82
H_{34}	34	5·20	5·39	5·44	5·44
N_2	28	4·28	4·37	—	4·20
O_7	112	17·12	—	—	—
$C_{40}H_{34}N_2O_7$..	654	100·00			

Attempts to obtain derivatives from this substance so as to fix its formula proved abortive. The solubility in alkalis and insolubility in acids appear to indicate that the body is a weak acid or a kind of phenol. Its solution in alkalis takes up oxygen slowly, and deposits green or black flakes, but no crystals; the solution in ammonia parts with all the ammonia present at 100°, and slowly loses it over sulphuric acid. No barium, silver, or lead salt could be obtained by double decomposition or treatment with the oxide. A mercury compound, however, is obtainable as a chocolate precipitate when the perfectly neutral solution of the substance in ammonia (obtained by leaving the ammoniacal solution over sulphuric acid for some days) is added to corrosive sublimate solution. A specimen of this substance gave the following numbers :—

A. 0·189 gram gave 0·1280 HgS. Hg = 58·40 per cent.
B. 0·2105 „ 0·049 AgCl. Cl = 5·76 „

From these numbers it appears probable that the chocolate precipitate is a mixture of calomel (formed by the reduction of the corrosive sublimate) and the mercury salt of some oxidation-product of the blue compound. The quantity of this chocolate substance obtained was too small for further examination.

When kept for two years in a sealed tube, the ethereal solution of the blue compound deposits black flakes, apparently arising from decomposition. Simultaneously with the blue compound, black flakes insoluble in ether are formed by the action of air on a solution of apomorphine in caustic potash. These are insoluble in acids, but somewhat soluble in dilute alkalis, and are probably identical with the flakes above mentioned formed by the further oxidation of an alkaline solution of the blue compound. Nothing fit for analysis could be obtained from these black flakes.

Admitting the accuracy of the empirical formula $C_{40}H_{31}N_2O_7$, the formation of this product from apomorphine may be taken as confirming the view deduced by one of us from previous researches, viz., that apomorphine is a derivative of the *di*-polymeride of morphine, and has consequently a formula containing more carbon than C_{34}.

Apomorphine is not the only body that is capable of giving rise to this colouring matter, deoxymorphine and diapo-dimorphine being both capable of producing it by the same treatment. It is noteworthy, however, that no "tetra" polymeride of morphine or codeine, no derivative from these polymerides, and no body of the class viewed in previous papers as derived from monomorphine or monocodeine is capable of yielding it, at least if the substance operated upon be perfectly free from apomorphine (tetrapo-dimorphine), deoxy-morphine, or diapo-dimorphine. It would therefore appear that the process which, for want of a better term, has been referred to under the name of "polymerisation," exerts a marked action on the chemical character of the substance operated on, as well as on the physical and physiological properties.

§ 2. *Action of Heat on Morphine Derivatives.*

When the aqueous hydrochloride of the base having the composition ($\overline{M}$ + HCl − H_2O), or the mixture of hydrochlorides of bases ($\overline{M}$ + HCl) and ($\overline{M}$ + 2HCl − $2H_2O$), &c., described in a former communication (this Journal, 1873, p. 215), is gently heated, the water evaporates, but the mass never solidifies, inasmuch as the gummy, anhydrous hydrochloride melts at a little above 100°; on continuing to heat, the mass darkens in colour, and at 150°—180° swells up, and gives off a powerful and peculiar odour; on dissolving the resulting mass in water, adding potash and distilling, a distillate containing *pyridine* is obtained. If the heating be interrupted before the temperature rises to 150°, little pyridine, or none at all, is formed; whence it appears probable that the monomorphine derivatives split up on heating into pyridine and some other substance (probably destroyed by the temperature employed), just as narcotine under analogous circumstances splits up into cotarnine and meconin (Matthiessen and Wright, *Phil. Trans.*, 1869, 667).

The pyridine obtained appears to be mixed with more or less methylamine, probably from the polymerisation by heat of the base employed (*vide infra*). The purest specimen obtained gave these numbers :—

0·1520 gram of platinum salt gave 0·0539 Pt. = 35·46 per cent.
Calculated for pyridine platinochloride, 34·67 per cent.

Other specimens gave 37—39 per cent. of platinum, and contained

so much methylamine, that the fishy smell of this base overpowered the tarry odour of pyridine, when potash was added to the mixture.

To prove that pyridine was really present in these mixtures, the platinochlorides were boiled with a large bulk of water for some days, when the characteristic platino-pyridine salt of Anderson was precipitated. Of this

0·3000 gram gave 0·1175 Pt. Pt. = 39·17 per cent.
Calculated for $C_{10}H_6Pt.N_24HCl$. = 39·75 „

In one experiment a product was obtained, which appeared to contain a higher homologue of pyridine (picoline, lutidine, &c.) but this portion was unfortunately lost, and the presence of these bodies could not be proved in any other specimen.

In a former communication (*loc. cit.*) it has been shown that by the prolonged action of hydrochloric acid on morphine, the monomorphine derivatives first produced become "polymerised," a tetra-base, $(\overline{M}_4 + 2HCl)8HCl = C_{136}H_{154}Cl_2N_8O_{24}8HCl$, being formed, together with apomorphine (tetrapodimorphine). Through the kindness of Messrs. Macfarlane, of Edinburgh, we have been enabled to examine the action of heat on the hydrochloride of this tetra-base, which is produced in some little quantity during the manufacture of apomorphine for pharmaceutical use. When it is treated in the same way as the monomorphine derivative above described, quantities of methylamine are obtained, but no trace of pyridine could be found by long-continued boiling of the platino-chloride. No appreciable quantity of ammonia appeared to be produced, the hydrochloride of the volatile base distilled off being wholly soluble in absolute alcohol. The platinum salt made from this gave these numbers:—

0·4500 gram gave 0·1890 Pt. = 42·00 per cent.
Methylamine platinochloride requires 41·68 per cent.

It is evident from these numbers, that no appreciable amount of pyridine could have been present, pyridine platinochloride requiring 34·67 per cent. of Pt.

On treating apomorphine (tetrapo-dimorphine) hydrochloride in precisely the same way, a just perceptible trace of methylamine was evolved, but no pyridine.

It hence appears that the three series of morphine derivatives, viz., the mono-, di-, and tetra-morphine series, differ in the way in which their hydrochlorides split up by the action of heat, the mono- series eliminating nitrogen in the form of pyridine; the di- series giving no appreciable quantity of any volatile base (at 150°—180°); and the tetra-series giving methylamine under the same circumstances.

In conclusion, we are desirous of expressing our obligations to

Messrs. Macfarlane and Co., of Edinburgh, for their kindness in furnishing us gratuitously, not only with the original morphine requisite for the preparations of the derivatives, &c., obtained by us, but also with a considerable quantity of apomorphine hydrochloride, and various bye-products obtained during its manufacture.

§ 3. By C. R. A. Wright, D.Sc.

Action of Silver Nitrate and Nitric Acid on certain Morphine and Codeine Derivatives.

It has been shown in previous papers that when certain bodies derived from polymerides of morphine or codeine are treated with silver nitrate and nitric acid, a *blood-red* liquid is formed; whilst when similar derivatives containing more hydrogen than that present in the normal morphine polymeride derivatives are treated in the same way, a bright *yellow* liquid is obtained; in some instances the amount of derivative at the operator's disposal was sufficient to enable him to isolate the colouring principles formed.

The derivative was dissolved in about 40 times its weight of boiling water, silver nitrate solution added in excess, and strong nitric acid in small quantity gently dropped into the hot liquid. Carbon dioxide and oxides of nitrogen were evolved with effervescence; all chlorine, bromine, or iodine associated with the compound examined was precipitated as silver salt, and a liquid was obtained, from which amorphous flakes deposited on cooling (after filtration whilst boiling). These flakes were almost insoluble in water in each case, but dissolved in boiling water acidulated with nitric acid, separating again as the liquids cooled; no trace of crystalline structure was noticeable in any instance, the flakes presenting under the microscope the appearance of strings of coalesced globules. Although the products obtained varied much in colour, yet comparatively little difference was noticed in the composition of the flakes. Neither treatment with ammonium sulphydrate nor with zinc and hydrochloric acid appeared to alter the substances in any way, nor did caustic alkalis produce any change other than solution of small quantities; from which it may be inferred that the substances are neither nitrates nor nitro-compounds. The following numbers were obtained:—

A. *Product from Chlorotetramorphine.*—This product, when purified by recrystallisation (if this term can be used in the case of a noncrystalline substance) from boiling dilute nitric acid, was of a bright scarlet colour, its concentrated solution being blood-red.

0·4760 gram gave	0·901	CO_2 and	0·159	H_2O.
0·4255 „		0·803 „	0·141	„
0·3805 „		0·2015 platinum.		

B. *Product from Tetramorphine.*—The purified flakes obtained in this case were brick-red, the solution being of a brownish red colour.

0·4250 gram	gave	0·847 CO_2	and	0·162 H_2O.
0·2415	„	0·4785 „		0 099 „
0·2845	„	0·1380 Pt.		

C. *Product from Tetracodeine.*—This much resembled that from tetramorphine.

0·4510 gram	gave	0·8750 CO_2	and	0·179 H_2O.
0·5405	„	1·049 „		0·216 „
0·4200	„	0·1900 Pt.		

D. *Product from the Base produced by action of Hydriodic Acid and Phosphorus on Codeine, at* 135°, viz. $[(\dddot{M} + H_8)_4 + 4HI - 12H_2O]$.—This was of a yellow tint, with a slight shade of orange; the solution was of a deep yellow colour, slightly inclining to orange.

0·2490 gram	gave	0·4800 CO_2	and	0·0980 H_2O.
0·3305	„	0·1545 Pt.		

	A.		B.		C.		D.
Carbon ..	51·62	51·45	54·36	54·04	52·90	52·93	52·57
Hydrogen	3·71	3·68	4·23	4·55	4·41	4·44	4·37
Nitrogen.	7·51		6·89		6·43		6·65

A agrees with the formula, $C_{21}H_{20}N_3O_{13}$; B approximates to $C_9H_8NO_4$; C is represented by $C_{19}H_{19}N_2O_{10}$; whilst D agrees with $C_{18}H_{17}N_2O_9$. All attempts to obtain derivatives by means of which these formulæ might be controlled proved abortive; fractional separation from hot dilute nitric acid did not cause the substances to separate into two dissimilar portions.

The mother-liquors from which the crude coloured flakes separated in these experiments were distilled with excess of caustic potash. No trace of pyridine was liberated, but ammonia and methylamine came over in some little quantity. The hydrochlorides of these two bases were separated by absolute alcohol, and the platinum salts made and analysed with the following results; contrary to what might have been expected, only traces of methylamine were formed in the case of specimen C from tetracodeine (from which the methyl groups originally present had not been eliminated), whilst larger amounts were produced in all the other instances where the original methyl groups had been expelled by the previous treatments to which the original alkaloïd had been submitted.

Specimen A (from chlorotetramorphine).

0·4765 gram gave 0·2005 Pt.

B (from tetramorphine).

0·4520 gram gave 0·1915 Pt.

C (from tetracodeine). Only just sufficient platinum salt was obtained for analysis, a considerable quantity of ammonium chloride being produced; the numbers indicate that the portion taken up by the alcohol was little but ammonium chloride.

0·5260 gram gave 0·2295 Pt.

D (from mother-liquors of D above).

0·4725 gram gave 0·1995 Pt.

E. The product of the action of hydriodic acid on morphine gave a deep yellow liquid, from which flakes separated, precisely resembling those from D above; through an accident, the quantity obtained of these flakes was too small for examination. The mother-liquors treated as the other specimens gave a platinum salt, of which

0·4415 gram gave 0·1875 Pt.

Calculated.		Found.				
		A.	B.	C.	D.	E.
For ammonium platinochloride	Pt = 44·27	—	—	43 63	—	—
For methylammonium ,,	Pt = 41 68	42·07	42·36	—	42·22	42 17

The brown product obtained during the extraction of morphine by the Robertson-Gregory process, and referred to on page 218 of this volume, when treated with silver nitrate and nitric acid, yielded flakes of a chocolate-red colour, which contained

Carbon	37·76	36·91
Hydrogen	3·20	2·92

The mother-liquors from which these flakes separated yielded much methylamine; the platinum salt obtained as above gave Pt. = 42·28 per cent.

XLV.—*Monthly Analytical Examinations of the Harrogate Spas*, 1872.

By R. Hayton Davis, F.C.S.

It has appeared to me that analytical examinations at short intervals of some of our principal Spas would be productive of valuable results, and, among other advantages, would probably assist in explaining discrepancies observable in different analyses of the same mineral water.

In the commencement of 1872 I began the following series of determinations, selecting for examination at monthly intervals two of the

most noted Harrogate Spas, viz., the "Old Sulphur Well" and the "Chloride of Iron Spa."

To make the results more complete, I have appended the monthly rainfall at Harrogate during the corresponding period.

The following were the results obtained; the quantities are in grains per gallon:—

Old Sulphur Well.

	Temp. in well.	Specific gravity.	Na.H.S.	Chlorine.	Total residue.	Rainfall each month in inches.
1872.						
January 31	—	1011·14	15·62	613·49	1029·28	4·50
February 29	46°	1011·37	15·86	616·93	1044·25	3·15
March 30	46°	1011·23	15·13	615·62	1012·01	2·31
April 30	47°	1010·31	16·35	614·45	1019·69	3·51
May 31	48°	1010·83	16·33	603·91	1034·20	1·64
June 29	50°	1011·95	16·48	616·22	1028·13	4·70
July 31	52°	1011·11	15·75	617·46	1056·26	5·90
August 31	52°	1010·84	16·24	612·46	1017·87	4·48
September 30	52°	1010·80	17·00	610·22	1041·14	5·18
October 31	50°	1011·42	15·76	619·62	1058·13	5·10
November 30	48°	1011·46	15·88	621·71	1067·10	5·23
December 31	47°	1011·47	15·98	625·32	1060·13	4·18
Average	48·9°	1011·16	16·03	615·62	1036·56	
Total	..	..	..	..	..	49·88
1854.						
Hofmann............	48·2°	1011·13	15·87	650·38	1095·51	—
1867.						
Muspratt............	—	—	16·83	655·27	1108·78	—

The water of the Old Sulphur Well rises naturally to the surface in a basin of irregular shape, about 2 feet in depth, and having a capacity of about 70 gallons.

The sodium sulphydrate, NaHS, was determined volumetrically at the well, the contents of a sp. gr. bottle taken; a little filtered solution of starch added; and solution of iodine (1 grain in 100 c.c) dropped in from a burette until the blue coloration was produced.

The chlorine was also determined volumetrically, first taking a weighed quantity of the water (about 10 c.c.); heating it in a flask to decompose the sodium sulphydrate; diluting; adding a few drops of solution of potassium chromate; and determining with a standard solution of silver nitrate.

The total saline constituents were estimated by evaporating a weighed quantity of the water (about 1000 grains) previously adding a weighed quantity of pure dried sodium carbonate, and the residue was dried in a platinum crucible at a temperature of 240° to 260° F. for one hour, then cooled under a beaker, and weighed.

Chloride of Iron Spa.

	Specific gravity.	$FeCl_2$.	FeO,CO_2.	Chlorine.	Total residue.
1872.					
January	1006·26	34·50	11·84	334·29	523·89
February	1006·47	33·77	11·12	340·19	517·89
March	1006·27	30·10	10·07	335·20	550·80
April	1006·17	28·97	11·33	339·80	557·09
May	1006·32	30·49	11·49	345·54	556·39
June	1006·33	29·88	11·17	346·69	555·43
July	1006·28	30·67	11·82	342·33	549·84
August	1006·12	26·97	9·73	339·68	540·96
September	1006·04	26·36	10·70	335·06	544·16
October	1006·31	32·27	10·32	334·10	532·04
November	1006·43	31·29	10·92	333·54	534·75
December	1096·25	31·62	10·07	329·53	528·45
Average	1006·27	30·57	10·88	338·02	540·97
1865.					
W. A. Miller	1005·09	14·49	11·62	283·25	465·47
1866.					
Muspratt	—	16·01	10·84	311·68	465·05

The chloride and carbonate of iron were estimated as follows:—The total quantity of iron was first determined volumetrically in 0·1 gallon of the water, using a standard solution of potassium permanganate; a similar quantity was boiled in a flask for an hour, then allowed to cool, filtered, and the quantity of iron in solution was estimated and calculated as chloride, the difference being regarded as originally existing in the water as carbonate, and calculated accordingly. In determining the chlorine a marked flask was filled, a few drops of ammonium sulphydrate added, the liquid then heated to dissipate the excess of ammonium sulphide, and the flask filled up to the mark when cold, with distilled water, and shaken; 10 c.c. of this were taken, diluted, and the chlorine determined volumetrically.

The history of this now celebrated Spa is peculiar. When first obtained by boring, in 1819, the water was free from ferrous chloride. Repeated analyses, extending over a period of 35 years, prove that it has been subject to considerable fluctuations in the amount of saline constituents. An analysis made by Dr. Hofmann in 1854 exhibits it as containing only 285 grains in the gallon, including ferrous carbonate 4·6 grains. From that date no analytical examination appears to have been made for 11 years, and in the interval this Spa had almost fallen into disuse. In the spring of 1865 it was first discovered that some remarkable change had taken place in the water, and analyses subsequently made by the late Dr. Muspratt and Dr. W. Allen

Miller, in the same year, first announced the presence of ferrous chloride in considerable quantity in this Spa.

At the present time not only is the quantity of ferrous chloride more than double, but the total solid constituents have considerably increased. Obviously a spring of such value requires periodic testing. The importance of such examinations is apparent, if we consider that it is quite a matter of conjecture at what period of the interval between 1854 and 1865 the iron chloride first made its appearance.

In comparing the two analyses, it will be noticed that the fluctuations in the proportions of chlorine and total residue in the two Spas do not correspond. This, no doubt, is due to the fact that while the water of the Old Sulphur Well springs naturally to the surface, the water of the Chloride of Iron Spa is collected in a well sunk several feet below the surface; the latter is consequently more liable to be affected by the rainfall by percolations from the surrounding strata.

In making these analyses great care was taken to insure accurate results. A sufficiency of the standard solutions was prepared in the first instance, and the same apparatus was used throughout.

The determinations of the chlorine and the total residue obtained were calculated for the gallon from the specific gravities; and temperatures were carefully noted, so that the results might furnish exact and trustworthy data with regard to these important springs.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

New Researches on the Silent Electrical Discharge. By P. and A. Thénard (Compt. rend., lxxvi, 1508—1514).

The silent discharge or "effluve" induces the combination of hydrogen and nitrogen, but unless the ammonia formed be removed, the action soon stops. Either strong sulphuric acid or water may be used to absorb the ammonia, and the presence of the latter does not interfere with the continuation of the combination. Ammonia gas is decomposed by the silent discharge, but only partially; a state of equilibrium is in both these cases reached, in which the mixture of H, N, and NH_3 undergoes no further change.

The vapour of water, which tends to prevent the ozonification of oxygen, is not injurious in many other cases. It is itself slowly decomposed by the silent discharge. Nitrogen and vapour of water slowly combine under the influence of the silent discharge, yielding probably ammonium nitrite.

Gaseous phosphoretted hydrogen is incompletely decomposed by the silent discharge. It first becomes spontaneously inflammable, and then deposits the solid phosphide. After removing the undecomposed phosphine by absorption, the further action of the discharge splits up the solid phosphide into phosphine and red phosphorus. The latter, being a conductor, causes the silent discharge to change into the spark and stops the experiment.

A mixture of phosphine and ethylene yields one of the phosphorus bases, various complicated secondary reactions going on at the same time.

Ethylene by itself condenses to a powerfully odorous liquid, soluble in ether, insoluble in water.

Hydrate of methylene (methyl ether) in presence of water decomposes into 1 volume of marsh-gas and 2 volumes of hydrogen, besides a strongly acid solution and a resinous body, soluble in alcohol, insoluble in ether.

M. J. S.

Action of Electricity on Flames, Liquids, and Powders (continued, *vide* Compt. rend. lxxvi, 1000). By Neyreneuf (Compt. rend., lxxvi, 1351).

The flame of pure hydrogen is attracted by the negative pole. With the carbon monoxide flame attraction takes place when both poles at once are presented to it. This result is considered important since the flame potash; and it is found that when the heat evolved in the formation of

contains no solid particles, and no water is formed. Carbon sulphide behaves in the same way. Alcohol acts like coal-gas. The flame of oil of turpentine burnt in a lamp is very much repelled by the current.

If either pole be perpendicularly directed close to the surface of water, oil, carbon sulphide, or oil of turpentine, contained in a good conductor, the liquid rises in a small cone, which subsides directly the surface is touched by the pole. Even with liquids which are bad conductors a similar cone is produced, if the pole be first dipped into the liquid and then slowly withdrawn.

Several substances, when in powder, exhibit phenomena similar to the above. When either pole is brought within a certain distance (not stated) of some of the blue drying sand used on the Continent, there is at first a centrifugal effect, and then, on a nearer approach, a centripetal, owing to the well-known action of the "electric wind." When the sand is touched by the pole and the latter is cautiously withdrawn a cone of sand is formed.

All these movements of flames, liquids, and powders, except those caused by the "electric wind," are considered to be due to a current of air which flows from the positive to the negative pole.

B. J. G.

On the Relation between Electric and Capillary Phenomena.

By G. Lippmann (Compt. rend., lxxvi, 1407).

The surface of a drop of mercury contained in a glass vessel and wetted with dilute sulphuric acid, quickly contracts, becoming more convex when it is made the negative electrode of a voltaic couple. It has been found by experiment that the contraction is due to a change in the capillary constant, this constant and the force of polarisation being continuous functions one of the other; also that an extension of surface produced mechanically is sufficient to polarise the surface as an electric current does.

W. A. T.

Heat Evolved in the Reactions of Chlorine and its Compounds.

By M. Berthelot (Compt. rend., lxxvi, 1514—1522).

1. *Action of Chlorine on Water.*—This action may take place in two different ways. The chlorine may simply dissolve in the water, in which case 35·5 grams of chlorine evolve about + 1·5 heat-units, or a reaction may take place between the chlorine and the water, by which hydrochloric acid and oxides of chlorine are formed, the numbers obtained then varying, but always being higher. This reaction is not caused by the presence of light, since similar differences were obtained in the dark; nor is it due to the existence of an allotropic modification of chlorine, since two samples yielding respectively + 1·79 and + 3·41 heat-units with water, gave identical numbers, + 12·66 and + 12·68, when absorbed by potash. It follows from this that chlorine-water does not always evolve the same quantity of heat when treated with

the chlorine-water is high, and consequently that disengaged on the addition of potash low, the hypochlorite formed does not show on titration the entire quantity of chlorine employed for the experiment. The reaction between the chlorine and water is probably brought about by the presence of a trace of a foreign body, which the author suggests may be hypochlorous acid.

Thomson (*Deut. Chem. Ges. Ber*, vi, 235) gives the number + 2·4 for the heat of solution of chlorine in water. This, on the authority of his own experiments, the author considers too high, and he rejects also all estimations which have been made by the aid of chlorine-water, which, as he shows, cannot be considered as always a liquid of the same nature.

2. *Action of Chlorine on Mercurous Chloride.*—The apparently simple reaction—

$$Hg_2Cl + Cl = 2HgCl.^*$$

is in reality complicated by the decomposition of water. Moreover, the above reaction is not instantaneous, but, except in presence of a large excess of chlorine, proceeds very slowly. No concordant results could be obtained as to its thermic value.

3. *Action of Chlorine on Stannous Chloride.*—The same is true of the reaction—

$$SnCl + Cl = SnCl_2.^*$$

In the absence of free hydrochloric acid the heat evolved per unit of chlorine increases with the proportion of chlorine used. The formation of hypochlorous acid in this reaction is very evident. Water decomposes stannous chloride into basic and acid salts, and it appears that part of the chlorine attacks the former, producing a hypochlorite or analogous salt. An excess of hydrochloric acid prevents the decomposing action of the water and concordant results are then obtained from each portion of gas successively added: 35·5 grams of chlorine evolving + 39 3 heat-units. Thomsen gives 36·9 heat-units, which indicates that his reaction was performed in a simple aqueous solution.

4. *Action of Chlorine on Ferrous Sulphate.*—Still greater variations were obtained in this case; the thermometer showed that the reactions continued for several minutes after the current of chlorine was stopped, and for half an hour afterwards the solution had the smell of oxides of chlorine, even in presence of an excess of acid. The curious incidental result was obtained that the mixture of ferrous sulphate with ferric chloride or nitrate absorbed a quantity of heat (1·7 and 1·78 heat units) corresponding with an almost complete double reaction between the two salts.

Thomsen gives + 23·5 as the heat evolved by the action of chlorine on ferrous sulphate. Berthelot's highest result, obtained in presence of a large excess of sulphuric acid, was 27·4, which he still considers too low. Thomsen's result does not agree with his own determination of the heat evolved by oxidation with permanganate, and still less with the author's number for the same reaction, whereas the number 27 4 agrees better with both and differs also in the right direction.

M. J. S.

* Old atomic weights

On Berthelot's Researches on Hydrochloric Acid.

By J. THOMSEN (Deut. Chem. Ges. Ber., vi, 717—719).

THIS is a criticism on Berthelot's recently published memoirs, "Sur la chaleur dégagée dans la Réaction entre les Hydracides et l'Eau," "Sur la Constitution des Hydracides dissous" (*Bull. Soc. Chim.*, xix, 351 and 385), and "Méthodes Calorimètriques" (*Ann. Chim. Phys.* [4], xxix, 94). The author points out that the results obtained do not agree with those calculated from the formula $Q = \frac{11620^{\circ}}{n}$ employed by Berthelot, their differences in some cases corresponding to 0·05°, 0·06°, and 0 07° in the reading of the thermometer; and he infers "that the researches of M. Berthelot on the development of heat of hydrochloric acid are extremely inaccurate," and that the results obtained give no support to the opinion that a stable hydrate $ClH + 8H_2O$ exists.

C. E. G.

The Affinity of Bromine for Oxygen.

By H. BAUMHAUER (Deut. Chem. Ges. Ber., vi, 598).

A SOLUTION of potassium chlorate was heated with bromine, and, after evaporation, no potassium bromate could be detected in the residue. Similarly no bromate was formed when bromine water was heated with potassium chlorate and a small quantity of nitric acid.

The affinity of bromine for oxygen thus appears to be less than the affinity of chlorine for oxygen.

T. B.

On the Action of Water on the Alkalis and Alkaline Earths. Constitution of Alkaline Solutions.

By BERTHELOT (Bull. Soc. Chim. [2], xx, 57—64).

I. *Ammonia.*—One gram-equivalent of the dry gas dissolved in 250—370 equivalents of water disengages 8·82 heat-units. The strong solution also evolves heat on dilution, the amount disengaged being in the inverse ratio of the quantity of water previously combined with the ammonia. In general terms $NH_3 + nH_2O$ disengages $Q = \frac{1 \cdot 27}{n}$ heat-units, which equation represents an equilateral hyperbola, as is the case with the hydracids. The fact that the dilution of ammonia produces only about one-ninth as much heat as is yielded by the hydracids is considered to be due to the formation in the former case of hydrates in a state of decomposition. After the addition of $9H_2O$ to NH_3 the heat evolved on further dilution becomes inappreciable.

The molecular volume of ammonia solution, $NH_3 + nH_2O$, may be represented by

$$V = 18n + 24 - \frac{1 \cdot 2}{n},$$

from which it will be seen that the dilution of ammonia solutions

causes dilatation, the amount of which diminishes as the dilution increases.* It is remarkable that this dilatation should be accompanied by development of heat, as these two physical effects are generally regarded as opposed to one another. With the fixed alkalis and with the hydracids contraction always takes place on dilution.

Similar phenomena are presented by the salts of the alkalis. The chloride and nitrate of ammonium expand when dissolved in a small quantity of water, and on dilution exhibit both contraction and absorption of heat. The corresponding salts of potassium and sodium produce contraction both when dissolved and when the solutions are diluted. In the formation of a salt from its acid and base mixed in dilute solution, a contraction takes place. In the case of ammonium salts this contraction is greater than for the corresponding potassium salts, although at the same time the heat of formation of the ammonium salt is the lower.

II. *Calcium, Barium, and Strontium.*—The heat of formation of the hydrates, and of their solution in water is given.

		Heat-units.
† $CaO + HO = CaHO_2$	disengages	$+ 7{\cdot}55$
$BaO + HO = BaHO_2$	,,	$+ 8{\cdot}81$
$SrO + HO = SrHO_2$	,,	$+ 8{\cdot}6$

The solution of the anhydrous bases in water disengages—

	Sat. sol.	Dil. sol.
CaO,	$+ 9{\cdot}05$	$+ 9{\cdot}5$ (about)
BaO,	$+ 13{\cdot}94$	$+ 14{\cdot}06$
SrO,	$+ 13{\cdot}4$	$+ 13{\cdot}4$

The solution of the hydrates disengages—

	Heat-units.
$CaHO_2$ (solution saturated)	$+ 1{\cdot}5$
$BaHO_2$,, ,,	$+ 5{\cdot}13$
$SrHO_2$,, ,,	$+ 4{\cdot}82$

The formation of the higher hydrates—

$BaHO_2 + 9HO$	disengages	$+ 12{\cdot}16$
$SrHO_2 + 9HO$	,,	$+ 12{\cdot}36$

The results with lime indicate the probable existence of an analogous hydrate.

Solution of the higher hydrates:—

$BaHO_2,9H_2O$ (solution saturated)	$- 7{\cdot}03$
$SrHO_2,9H_2O$,, ,,	$- 7{\cdot}54$

The closeness and even the order of the numbers for the three alka-

* The fact of the expansion of ammonia solutions on dilution is pointed out by Gerlach (*Specifische Gewichte der Salzlosungen*, 1859), but the numbers which he gives do not agree with the above formula.—M. J. S.

† The formulæ and numbers are given as they appear in the original, Berthelot employing the old atomic weights.

line earths are quite in accordance with their relations to one another in other respects.

III. *On the Constitution of Alkaline Solutions.*—All the known facts indicate that solutions of the caustic alkalis contain hydrates higher than MHO, and it is interesting to observe how very different methods frequently point to the same composition for these hydrates. The hydrates $KHO.2H_2O$, $2NaHO.3H_2O$, and $2NaHO.7H_2O$ are known in the crystalline state. The vapour-tension of the alkaline solutions indicates the presence of the hydrates $KHO.2H_2O$ and $2NaHO.3H_2O$, and the depression of their freezing point leads to the same result.

The author's thermochemical researches render probable the existence of several hydrates, the formation of which is apparently completed when $7H_2O$ have been added to KHO and $6H_2O$ to NaHO. The precipitation of the alkaline chlorides by the corresponding hydrates shows that KHO has a special affinity for $6H_2O$ and NaHO for $4H_2O$. The author considers that the existence of these hydrates in dilute solutions, and their non-existence or incomplete formation in concentrated solutions, will explain the numerous reciprocal actions exhibited by the caustic alkalis, and that it is the energy possessed by the lower hydrates, as evinced by the heat of dilution, which performs the necessary work for the accomplishment of the inverse reaction.

M. J. S.

Note on the Decomposition by Heat (Dissociation) of Red Oxide of Mercury. By H. Debray (Compt. rend., lxxvii, 123—126).

The author objects to the conclusions drawn by J. Myers (see p. 603 of this volume) from his experiments on the decomposition of mercuric oxide by heat, on the ground that the vapour of mercury being constantly removed by condensation in the cooler portions of the apparatus, the conditions for the attainment of a maximum tension of decomposition did not exist. In order to study the real phenomena of decomposition, it would be necessary to heat the substance in an apparatus of which every portion should be at the same temperature.

Myers found that at about 400° the tension of the oxygen exhibited no maximum, and that the decomposition proceeded with almost the same rapidity after prolonged heating to 440° as at first. Moreover, on cooling, the tension of the oxygen did not diminish. The author, on the contrary, found that when a sealed tube containing mercury and oxygen was heated to 440°, the oxygen was almost entirely absorbed, and that even on rapidly cooling the tube, the combination completed itself before a temperature could be reached at which the elements would be without action on one another. This difference is evidently due to the fact that in Myers's experiments the tension of the mercury vapour was very low compared with that of the oxygen. That an apparent maximum tension was obtained at temperatures below 350° was probably due to the very slow rate at which decomposition proceeds at those low temperatures.

The experiments of Wurtz on the determination of the vapour-density of phosphorus pentachloride by volatilising it into a large

quantity of the vapour of the trichloride are also referred to, the suggestion being put forward that the apparently diminished decomposition of the pentachloride under these circumstances might be due to its decomposing more slowly in presence of an inert gas than when heated alone, rather than to any specific power of the trichloride to prevent the decomposition, to do which it would theoretically be powerless. M. J. S.

On the Heat of Combustion of Formic Acid. By BERTHELOT (Compt. rend., lxxvi, 1433—1441).

THE experiments detailed in this paper were undertaken with the view of ascertaining if the heat of combustion of formic acid, as determined by Thomsen, was correct. This chemist, by oxidizing formic acid with potassium permanganate, had found the number 60·193 heat units for one equivalent, CH_2O_2, whereas Favre and Silberman, by the direct combustion of the acid in oxygen, had found 96 units.

The author first prepared a large quantity of pure crystalline formic acid, which was found to melt at 8·6°, then carefully determined the heat of fusion of the acid (— 2·43) and the heat of neutralisation, CH_2O_2 in solution, + $\frac{1}{2}(K_2O)$ in solution, which was + 12·98.

Formic acid is decomposed at the ordinary temperature by concentrated sulphuric acid into carbonic oxide and water, but the reaction, which goes on rapidly at first, is not complete until after the lapse of some time, about a day, so that the thermometric observations must be made at the commencement of the reaction. For this purpose the heat, (Q_1), evolved by the mixture of formic and sulphuric acid during the first ten minutes of the reaction was observed; it was then largely diluted with water and the calorific effect again observed, (Q_2), and from these data and that previously obtained on adding to sulphuric acid, first water and then formic acid, $(Q + q)$, the heat developed by the decomposition of the formic acid, $= Q_1 + Q_2 - (Q + q)$ can be calculated; and since the amount of formic acid decomposed is known, by measurement of the carbonic oxide produced, the heat developed by the decomposition of an equivalent of pure formic acid, CH_2O_2, into carbonic oxide and water can be ascertained. This is 1·38 heat equivalents; according to the results of Thomsen it should be — 6·6, a difference of nearly 8 heat-units.

The action of bromine, chlorine, and the hypochlorites on formic acid is too slow for thermometric observations, and the use of potassium permanganate introduces great complications, since the precipitated oxide of manganese has not a constant composition, moreover, it carries down with it varying proportions of potash. The author therefore pursued the following course: he first determined the heat of combustion of oxalic acid by passing a known weight of chlorine into a solution of potassium hydrate, and subsequently converting this chlorine into hydrochloric acid by means of oxalic acid, and then that of the reduction of potassium permanganate by oxalic acid in presence of a large excess of sulphuric acid; from the results of these two experiments he was able to calculate the excess of heat disengaged during the oxidation by means of potassium permanganate and sulphuric acid over that de-

veloped by the same oxidation effected by free oxygen, this was found to be 4·69 for each equivalent of oxygen, (O = 8 ?). He then determines the heat developed during the oxidation of potassium formate by permanganate of potassium, adding sulphuric acid and a known weight of oxalic acid which decomposes and dissolves the precipitated manganese oxide, thus avoiding the complication introduced by the presence of this substance. From the results it is easy to calculate the heat of combustion of formic acid by means of free oxygen; this the author finds to be 69·9, a result agreeing with that obtained by the transformation of the acid into carbonic oxide and water.

The author concludes his paper by observing,—1. That the production of formic acid from carbonic oxide and water is accompanied by absorption of heat, so that the energy consumed in the synthesis of formic acid from carbonic oxide and an alkaline hydrate is derived from the action of the acid on the alkali. 2. The heat of combustion of formic acid is 140 less than that of acetic acid, being nearly proportional to the relation which exists between acetic acid and its homologue, butyric acid (143 + 2). 3. The change of liquid formic acid into carbonic acid gas and hydrogen should only give rise to a feeble thermic effect or none at all. 4. The formation of marsh gas by the dry distillation of barium formate gives rise to a disengagement of heat equal to about + 54 units. All these metamorphoses are produced at the expense of the excess of energy which formic acid possesses compared with the carbonic acid and hydrogen. They show how the principal secret of the synthesis of organic compounds consists in the formation of the first terms, those namely which are accompanied by an absorption of heat, and which subsequently give rise to other principles, with development of heat, that is to say, according to the law of chemical combination.

C. E. G.

Heat Developed during the Formation of the Potassium and Sodium Salts of Acetic and Trichloracetic Acid. By B. Louguinine (Deut. Chem. Ges. Ber., vi, 563—564).

These determinations were made in order to ascertain what influence the introduction of an atom of a haloid into an acid radical has on the heat of neutralisation, since it would seem, from the investigations of Thomsen, that acids belonging to the same type develop the same amount of heat during neutralisation. The methods were substantially the same as those which the author had previously employed, in conjunction with Berthelot, for determining the heat developed by the decomposition of the chlorides and bromides of phosphorus. The alkaline solution used contained from 0·75 to 2 per cent., and it was previously ascertained that trichloracetic acid was not decomposed either by water or by a 2 per cent. alkali solution.

The formula employed for calculating the heat of neutralisation of 163·5 grams of trichloracetic acid was $Q = \frac{163 . s(P . c . s + a)(t_1 - t)}{p}$, in which 100P = weight of the liquid in the calorimeter; $c . s$ its heat capacity; a the weight of the whole of the apparatus multiplied by

its specific heat; $t_1 - t$ the elevation of temperature during the reaction, corrected by Pfaundler's formula; p the weight of the trichloracetic acid employed.

The heat developed by the solution in water of pure acetic acid, melting at 16°·5 and boiling at 118°, was found to be 369 units, and for pure trichloracetic acid 2900 units; on dissolving acetic acid in potash-solution, 13499 units, and in caustic soda 13468, whilst trichloracetic acid gave 14235 in potash and 14166 in soda. Thus the heat developed during the formation of the potassium and sodium salts depends not only on the type or constitution of the acid, but also on the elements it contains.

C. E. G.

Thermochemical Researches on the Solution of various Solid, Liquid, and Aëriform Substances in Water. By J. THOMSEN (Deut. Chem. Ges. Ber., vi, 710—717).

THIS paper consists principally of the tabulated thermochemical results of a number of determinations made at various times at a temperature of about 18°. They are divided into eleven groups, namely:—

1. Crystalline chlorine, bromine, and iodine compounds. 2. Liquid chlorine and bromine compounds (including bromine itself). 3. Nitrates. 4. Sulphates. 5. Acetates. 6. Potassium salts. 7. Sodium salts. 8. Barium salts. 9. Crystalline acids. 10. Liquid acids. 11. Aëriform substances.

The author observes that the greater number of salts absorb heat on solution, but yet that there are many salts which, even when united with the largest amount of water of crystallisation, develop heat when dissolved. The difference between the thermic results with the corresponding nitrates and sulphates of the alkalis is almost constant, but not so with the chlorides, bromides, and iodides. All the crystallised acids examined absorbed heat when dissolved, whilst the liquid acids on the contrary developed heat. It was found that the latent heat of salts increases with the amount of water, so that aqueous solutions of salts which absorb heat when dissolved, also cause absorption of heat when their solutions are diluted; this is well illustrated by the numbers obtained with sodium sulphate.

The concluding part of the paper is occupied in discussing the probable cause of the difference in the thermic results obtained on dissolving a salt when united with different amounts of water of crystallisation.

C. E. G.

The Solubility of Saline Mixtures. By FR. RÜDORFF (Deut. Chem. Ges. Ber., vi, 482—486).

WHEN water is saturated with two salts which can exert no chemical action on one another (the same acid or base being common to both), the solubility of each is found to be diminished. For example, 100 c.c. of water at 19° dissolve 29·1 grams of NH_4Cl and 173·8 grams of NH_4NO_3 together, whereas 100 c.c. of water at the same temperature

can dissolve 37·0 grams NH_4Cl, or 183·0 grams NH_4NO_3 singly. In some cases the proportion of each salt which dissolves is not influenced by the presence of a large excess of either salt, but in other cases it was found that the presence of a large excess of one salt will almost prevent the solution of another. This is well illustrated by the behaviour of a saturated solution of the double salt, $(NH_4)_2SO_4.CuSO_4$. Ten grams of this solution contain at 16°, 0·855 gram of $CuSO_4$ and 0·712 of $(NH_4)_2SO_4$, but if one-fifth of its weight of $CuSO_4$ be dissolved in it by the aid of heat, it will be found that the solution, when cold, contains 1·585 grams of $CuSO_4$ and only 0·565 of $(NH_4)_2SO_4$. If, on the other hand, one-fifth of $(NH_4)_2SO_4$ be dissolved by the aid of heat in 10 grams of the solution, and the whole be allowed to cool, it will be found that the liquor retains only 0·177 gram of $CuSO_4$, but 1·816 of $(NH_4)_2SO_4$. If a larger amount of ammonium sulphate be employed, the quantity of copper sulphate remaining in solution may be still further reduced.

100 grams of water at 16·1° dissolve 76·2 grams $CuCl_2$ or 121·1 grams $CuCl_2 + 2H_2O$.

For the numerical details of the experiments made with various salt the original paper must be consulted. T. B.

The Solubility of Saline Mixtures. By F. RÜDORFF (Deut. Chem. Ges. Ber., vi, 643—646).

THE object of the experiments detailed in this paper was to ascertain whether a saturated solution of salts containing two bases and two acids is the same in whatever manner the bases and acids are combined; for instance, whether a saturated solution made from a mixture of KNO_3 and NH_4Cl is the same as one made from a mixture of KCl and NH_4NO_3. The results obtained with a mixture of NH_4Cl and KNO_3 indicate that at 14·8°, 100 grams of water dissolve 38·8 grains NH_4Cl and 34·2 of KNO_3, and, as might be expected, the addition of either of the pulverised salts to the solution caused no change of temperature. With mixtures of KCl and NH_4NO_3, however, the results were found to vary with the proportions of the two salts in the mixture, and the addition of either of the salts to the solution causes a change of temperature; but the addition of KNO_3 or NH_4Cl produces no such effect. It was observed that the addition of KCl or NH_4NO_3 to the saturated solution of NH_4Cl and KNO_3, produced a change of temperature.

The following pairs of salts gave a similar result:—

$$K_2SO_4 + NH_4Cl \text{ and } KCl + (NH_4)_2SO_4.$$
$$K_2SO_4 + NaCl \text{ and } KCl + Na_2SO_4.$$
$$KNO_3 + NaCl \text{ and } KCl + NaNO_3.$$
$$NaNO_3 + NH_4Cl \text{ and } NaCl + NH_4NO_3.$$

But the pairs—

$$KNO_3 + (NH_4)_2SO_4 \text{ and } K_2SO_4 + NH_4NO_3.$$
$$NaH_4Cl + Na_2SO_4 \text{ and } (NH_4)_2SO_4 + NaCl.$$
$$NaNO_3 + K_2SO_4 \text{ and } Na_2SO_4 + KNO_3.$$

do not give saturated solutions of definite composition.

C. E. G.

The Decomposition of Explosive Bodies compared with the Phenomena of Supersaturation. By J. Champion and H. Pellet (Compt. rend., lxxvii, 53—57).

The title explains sufficiently the contents of this paper.

W. A. T.

Determination of Boiling Points at the Normal Pressure. By H. Bunte (Ann. Chem. Pharm., clxviii, 139—142).

Contains the description and drawing of a simple apparatus, by means of which the boiling point of a liquid can be determined at the normal pressure if the atmospheric pressure be below 760 mm.

C. S.

Inorganic Chemistry.

Behaviour of Ozone to Water. By C. Rammelsberg (Deut. Chem. Ges. Ber., vi, 603—605).

Ozone from various sources was passed through water, but nothing that could be called ozone-water or a solution of ozone, was obtained. A sample of "concentrated ozone-water" prepared by Krebs, Kroll, and Co., contained 0·16 per cent. of chlorine, and a similar solution may be obtained by passing air first through a solution of calcium hypochlorite and afterwards through water.

T. B.

Notice on the Mutual Action of Hydrochloric Acid and Oxygen on certain Metallic Bodies in producing a Continuous Stream of Chlorine (Deacon's process). By M. Lamy (Bull. Soc. Chim. [2], xx, 2—4).

If hydrochloric acid gas and air be passed over cupric sulphate, oxide, or chloride, over the oxides of iron, manganese, lead, or chromium, or over bodies which contain any of these substances even in minute quantity, a continuous current of chlorine is produced, provided the temperature be sufficiently high. If cupric sulphate be used, the oxide, and finally the chloride, is produced, but in a proportion extremely small compared with the amount of chlorine set free. The amount of chlorine liberated bears some proportion to the rate of the current; it is larger if but a small quantity of hydrochloric acid be used with a large proportion of oxygen, but is only approximately in the inverse ratio of the square root of the amount, as given by Mr. Deacon. A mixture of hydrochloric acid with 60 parts of air or oxygen containing 4 per cent. of acid, yields, when passed over copper salts, from 20 to 95 per cent. of chlorine at a temperature of 440°, but none at 360°. Oxides of manganese, iron and chromium give but half that quantity at the above temperatures, but at the melting point of glass, from 50 to 75 per cent. Pumice-stone yields 15 per cent. at 440°, and 30 per cent. at a red heat. Grey pumice gives less than white. Silica at a red heat also

causes the reaction, owing to the presence of a small quantity of iron. A mixture of silica and an alkaline chloride heated in a current of air also yields chlorine (de Lalande and Prud'homme), but in smaller quantity as the materials are purer. W. R.

Reply to Criticism on the Authors' Method of Preparing Chlorine. By DE LALANDE and PRUD'HOMME (Bull. Soc. Chim. [2], xx, 74—76).

LAMY (see above) suggests that the authors' method of preparing chlorine by means of a mixture of hydrochloric acid and air acting on silicates, or by the action of air on a mixture of silica and chlorides, owes its success to the presence of ferric oxide and other impurities, which have been pointed out by Deacon as active in this respect. But the reaction is not limited to the cases in which silica is employed; oxygen displaces the chlorine from chlorides, at a red heat, provided any fixed acid capable of uniting with the base thus formed is present.

The experiment has been repeated with sodium chloride and boric acid free from all impurities, save other chlorides or fixed acids. The mixture was kept at a red heat, and a current of dry air passed over it for three hours. In that interval 15 per cent. of the chlorine was evolved. Sodium chloride heated with 5 per cent. ferric oxide gave off less than half a per cent. of its chlorine.

B. J. G.

Preparation of Iodides and Bromides. By C. RICE (Pharm. J. Trans. [3], iv, 5).

IODIDES and bromides, especially the former, prepared by the intervention of iron, are rather prone to develop, in the course of time, free hydracids and halogens, unless the salt has been exposed to a high temperature, which is, of course, inadmissible in the case of ammonium salts. The following is given as a working formula for ammonium bromide.

Dissolve 4 troy ounces of potassium bromide in 6 fluid ounces of boiling water, and 3 troy ounces of ammonium sulphate in $4\frac{1}{2}$ fluid ounces of boiling water. Mix the solutions while hot, and leave the mixture to cool. Then add $1\frac{1}{2}$ ounce of alcohol and set aside for 24 hours. Pour off the clear liquid, wash the precipitate with a small quantity of a mixture of 1 part alcohol and 4 parts water, and concentrate to the point of crystallisation.

In working upon a larger scale, it is advisable to redissolve the first crop of crystals of ammonium bromide in a small quantity of very cold water, allowing as short a time as possible for the solution. The greater part of the accompanying potassium sulphate, which has crystallised out at the same time, will remain undissolved at first, and may be removed, when the solution may be again concentrated until a pellicle forms. The successive crops of crystals are first drained, then dried at a very gentle heat on blotting-paper laid upon porous bricks. J. B.

On some Compounds of Zirconium. By S. R. Paijkull (Bull. Soc. Chim. [2], xx, 65—67).

Zirconium chloride combines with phosphorus pentachloride, forming $2ZrCl_4.PCl_5$, which melts at about 240°, and boils at 325°.

A double chloride of zirconium and sodium has the formula, $ZrCl_4.2NaCl$. Zirconium chloride absorbs ammonia gas, forming apparently $ZrCl_4.4NH_3$.

The sulphide (impure) obtained by the action of dry hydrogen sulphide on the chloride is easily soluble in nitric acid, with separation of sulphur. Chlorine attacks it only when heated.

Hydrated oxychlorides were obtained of the formulæ $2ZrOCl_2.13H_2O$, and $ZrOCl_2.8H_2O$. It is stated that the tetrachloride does not exist in solution.

The hydrate dried at 100° is ZrH_2O_3, whether precipitated hot or cold.

The crystallised sulphate contains $4H_2O$, of which it loses three-fourths at 100°.

The arsenate has the composition, $4\left[\left.\begin{matrix}ZrO\\H\end{matrix}\right\}AsO_4\right] + 3H_2O$. It forms a white powder, insoluble in water and in hydrochloric acid.

The orthophosphate is of complicated and probably variable composition.

M. J. S.

Action of Copper on Ammonium Sulphides. By K. Heumann (Deut. Chem. Ges. Ber., vi, 748—752).

Copper turnings digested in colourless solution of ammonium sulphide, free from hydrosulphide, cause an evolution of hydrogen gas, and soon become covered with crystals of cuprous sulphide. On adding water or hydrochloric acid to the supernatant liquid, a precipitate containing copper is thrown down. The solution being colourless, this could not have been in the form of the red compound described by Peltzer, Bloxam, and Vohl, though probably a similar compound containing less sulphur may exist.

The cuprous sulphide obtained by this process consists chiefly of very slender needles of grey colour and metallic lustre, which undergo some change on exposure to air, in consequence of oxidation.

Cupric oxide, treated with ammonium monosulphide, yields a black precipitate, consisting chiefly of Cu_2S, but containing much CuS. The supernatant liquid gives a precipitate of sulphur when mixed with hydrochloric acid.

Silver immersed in yellow sulphide of ammonium, becomes coated with sulphide, but in the monosulphide it remains unaffected.

W. A. T.

Crystalline Mercurous Iodide. By P. Yvon (Compt. rend., lxxvi, 1607—1609).

By heating the required proportions of mercury and iodine in a closed flask on the sand-bath, at a temperature not exceeding 250°, the author has obtained mercurous iodide condensed on the upper part of the

vessel in well defined rhombic crystals, of a magnificent garnet-red colour, which become yellow on cooling. If carefully heated, the compound sublimes unchanged, but if rapidly heated, the crystals melt at 290° to a black liquid, which boils at 310°, mercury being given off, and a pale yellow crystalline sublimate obtained, which appears to be an oxyiodide, perhaps of the composition $6HgO.7HgI$. H. E. A.

On Some Ammoniacal Salts of Silver. By M. O. WIDMAN (Bull. Soc. Chim. [2], xx, 64).

THE following salts were obtained by dissolving the silver salts in ammonia, and crystallising the solutions over a mixture of quicklime and sal-ammoniac, or by saturating the salts with ammonia gas:—

Ammonio-argentic Tungstate, $(AgN_2H_6)_2WO_4$.—Tabular crystals permanent in the air. Prepared in the dry way, it forms a white, bulky powder. Soluble in water; the solution soon decomposes. Loses its ammonia at 60°.

Ammonio-argentic Molybdate, $(AgN_2H_6)_2MoO_4$.—Probably isomorphous with the preceding salt. Obtained in the dry way, it forms a white powder, which loses its ammonia at 65°.

Ammonio-argentic Arsenate, $\left.\begin{matrix}2(AgN_2H_6)\\ Ag\end{matrix}\right\} AsO_4$.—Colourless needles, very soluble, easily lose their ammonia in the air, becoming reddish-brown. An ammonio-argentic antimonate could not be prepared.

M. J. S.

Action of a Sulphur-spring on Cast Iron. By E. PRIWOZNIK (Ann. Chem. Pharm., clxviii, 126—132).

THE mineral-water of Deutsch Altenburg contains a considerable quantity of hydrogen sulphide and sodium chloride, together with carbon dioxide, magnesium and calcium carbonates, calcium sulphate, calcium chloride, magnesium chloride, sodium sulphate, silicic acid, and a small quantity of sodium iodide. If the water be exposed to the air, sulphur separates out and it becomes milky, and on the bottom of the well a dark slimy precipitate is found, containing ferrous sulphide. A cast-iron tube, through which it has been conveyed for twelve years, showed three distinct layers. The outer one consisted of unchanged cast iron, while the middle one contained less iron and more graphite, and exhibited a laminar crystalline texture, and was very brittle. The thin inner layer, which was in some parts wanting, had the following composition:—

Ferric hydroxide, $Fe_2O_3.Fe_2(OH)_6$	81·08
Sulphur	12·29
Ferrous sulphide	4·48
Hygroscopic water	0·57
Nickel, cobalt, magnesia, soluble and insoluble silicic acid, traces of carbon ammonium chloride, sodium chloride, and loss	1·58
	100·00

Mineralogical Chemistry.

Constitution of Vesuvian. By C. RAMMELSBERG (Deut. Chem. Ges. Ber., vi, 783).

AN examination of several varieties of vesuvian showed that those kinds which are poor in iron contain only Fe (*ferricum*), while those rich in iron contain a certain proportion of Fe (*ferrosum*).

In all varieties of vesuvian R is to Si as 1 to 3·5, and in all the varieties which the author has now examined, that from Wilui excepted, R is to R as 1 to 4, and (K,H) is to R as 1 to 2·66. In that from Wilui, R is to R as 1 to 4·5, and (K,H) is to R as 1 to 9. Hence the general formula for most kinds of vesuvian is $H_3R_8R_2Si_7$, and that of Wilui is $HR_9R_2Si_7$.

T. B.

A New Source of Struvite. By R. OTTO (Deut. Chem. Ges. Ber., vi, 783).

CRYSTALS of this rare mineral were discovered in a mass of decomposing excrement which was found at a depth of about seven feet under the pavement of the old Knochenhauer Strasse, in Brunswick.

The author intends to subject this mineral to a careful examination.

T. B.

A Natural Compound of Ferric and Cuprous Oxides, and the Artificial Production of Atacamite. By M. C. FRIEDEL (Compt. rend., lxxvii, 211—214).

A MINERAL found by the author in the collection of the Ecole des Mines, and labelled "*Graphite on White Lithomarge, Catherinebourg, Siberia.*" It consisted of Fe_2O_3, 47·99; Al_2O_3, 3·52; Cu_2O, 47·45, corresponding with the formula $(Fe,Al)_2O_3Cu_2O$.

Its density is 5·07; hardness 2·5; streak greyish black; cleaves easily into very thin laminæ, which are perfectly opaque; soils the fingers; dissolves easily in acids.

Finer specimens were subsequently found in the collection of the museum of natural history. The name *delafossite* is proposed for it.

Attempts to prepare this mineral artificially by heating a solution of ferric chloride with cuprous oxide to 250° in a sealed tube, resulted instead in the formation of atacamite, in crystals large enough for the measurement of their angles. The iron was all precipitated. This is suggested as being very possibly the natural mode of the formation of atacamite, especially as this mineral is frequently accompanied by ferric oxide.

M. J. S.

Gold from Vancouver Island and West Africa.

By F. WIBEL (Jahrbuch für Mineralogie, 1873, 214).

THE specimen from Vancouver Island is a crystal about 7 mm. long, weighing 26·7 grams and having the form of a rhombic dodecahedron (∞O) prismatically elongated in the direction of one of its axes, as in a specimen from the Ural described by G. Rose. Sp. gr. 18·5 at 22°. Its analysis gave—

Gold.	Silver.	Copper.	Iron.
91·86	6·63	1·00	0·51 = 100

No mercury, lead, or other metals were found in it.

The specimens from West Africa, analysed by K. Wibel, consisted—*a*. Of gold in grains; *b*. Of gold-dust; *c*. Of gold obtained by washing from a flesh-coloured clay in the neighbourhood of Elmina.

	a.		*b*.			*c*.
Gold	89·40	87·91	97·23	96·40	92·03	97·81
Silver....	10·07	11·40	2·77	3·60	5·82	2·19
Copper ..	0·53	0·69	—	—	2·15	—
	100·00	100·00	100·00	100·00	100·00	100.00
Sp. gr. ..	14·63	16·20				

Other specimens of West African gold containing 4·15 and 25 p.c. of copper, and variable quantities of zinc, tin, and lead, were found to be adulterated with brass.

H. W.

Notices on Uranium Minerals. By A. WEISBACH (Jahrbuch für Mineralogie, 1873, 296—314).

THE first of these notices contains analyses by Winkler of a uranium ore from Schneeberg, occurring in beautiful egg-yellow capillary crystals, of sp. gr. 3·87. These analyses show that the mineral is identical with uranotil from Wölsendorf in Bavaria, analysed by Boricky (*Jahrbuch*, 1870, 780).

	From Wölsendorf, Boricky.	From Schneeberg, Weisbach.	
SiO_2	13·78	13·02	14·18
P_2O_5	0·45	—	—
U_2O_3	66·75	63·93	62·84
Al_2O_3,Fe_2O_3	0·51	3·03	2·88
CaO	5·27	5·13	5·49
H_2O	12·67	14·55	13·79
	99·43	99·66	99·48

These analyses lead to the formula $U_2O_3.SiO_2 + H_2O$.

According to v. Zepharovich, the needles of uranotil from Wölsendorff are rhombic, and exhibit the combination $\infty P . \infty\breve{P}\infty . m\breve{P}\infty$. The angle $\infty P : \infty P$ is approximately 164°. Sp. gr. 35.

The second notice contains descriptions of the minerals—

Trögerite	$3U_2O_3 . As_2O_5 + 12H_2O$.
Walpurgin	$5Bi_2O_3 . As_2O_5 + 3U_2O_3 . As_2O_5 + 10H_2O$.
Zeunerite	$CuO . 2U_2O_3 . As_2O_5 + 8H^2O$.
Uranospinite	$CaO . 2U_2O_3.As_2O_5 + 8H_2O$.
Uranosphærite	$Bi_2O_3 . U_2O_3 + H^2O$.

from the "White Hart" mine, near Schneeberg, the analyses of which have already been given in the present volume (p. 606).

Trögerite forms lemon-yellow monoclinic crystals, scaly by predominance of the clinopinacoïd, bearing a general resemblance to the crystals of heulandite, and, like the latter, having a nacreous lustre on the clinopinacoïd faces.

Walpurgin is mostly lemon-yellow, honey-yellow, or wax-yellow, sometimes however straw-yellow. The crystals have the character of the ordinary crystallisation of gypsum. The most highly developed faces are, as in trögerite, those of the clinopinacoïd, but they have an adamantine rather than a nacreous lustre. The projecting summits of the crystals are often serrated.

Zeunerite forms emerald-green or apple-green quadratic crystals, of pyramidal, tabular, or scaly character, consisting of the prism, the base, and a very acute pyramid. The basal faces have a nacreous lustre, and correspond with the direction of a perfect cleavage. Zeunerite is, therefore, not only analogous in chemical composition to ordinary copper-uranium mica (torbernite), but likewise isomorphous and isoclastic with it. The two minerals are, indeed, deceptively similar to one another in appearance.

Uranospinite forms siskin-green scaly crystals having a square or rectangular transverse section; their optical characters show that they belong to the rhombic system. The cleavage-planes run parallel to the plane of the scales, and notwithstanding the perfection of the cleavage, they exhibit but little tendency to nacreous lustre. Uranospinite probably belongs also to the family of the uranium micas, being indeed the arsenate analogous to lime-uranite (autunite).

Uranosphærite forms orange-yellow or egg-yellow nodules, roughly or finely drusy, and having a dull or faint satiny lustre. Under the microscope the drusy surface resolves itself into an aggregate of acutely pyramidal crystals, sticking out from the nodules like the bristles of a hedge-hog. The fractured surface exhibits a fatty lustre, and a concentrically scaly structure.

All five species are somewhat lighter-coloured when pulverised, and are intermediate in hardness between gypsum and calcspar. Their specific gravities, according to the mean of several determinations at 9°, are—

Trögerite.	Walpurgin.	Zeunerite.	Uranospinite.	Uranosphærite.
3·23	5·64	3·53	3·45	6·36

Trögerite is therefore the lightest, and uranosphærite the heaviest of the five.

With regard to succession in time, walpurgin and trögerite appear to

be the oldest formations, then follows uranosphærite, then zeunerite, and lastly uranospinite. Weisbach has also observed a regular aggregation between trogerite and zeunerite, the base of the latter running parallel to the clinopinacoid of the former, and a transverse axis of the latter to the principal axis of the former. Zeunerite likewise aggregates regularly with uranospinite in the manner observed by Breithaupt, in aggregates of the two well-known uranium micas, torbernite and autunite. H. W.

Lime Uranite in the Phosphorite of Carceres.

By F. WIBEL (Jahrbuch für Mineralogie, 1873, 242—244).

THIS phosphorite, which occurs in the range of mountains separating the Spanish province of Carceres from Portugal, exhibits, for the most part, the appearance of the ordinary Estremadura phosphorite, but is less coloured and mostly quite white. Ferric hydrate and dendrites of manganese oxide occur in it here and there, also druses of quartz crystals and numerous tabular crystals of apatite (0P.∞P.∞P2), several centimeters broad. Lime uranite occurs sparingly but in distinct crystalline tablets, exhibiting the ordinary quadratic combination oP.P.∞P, seldom isolated, mostly grouped together in the phosphorite mass, or at the surfaces of the apatite crystals. Their colour varies between the characteristic yellow-green of the mineral and a bright grass- or emerald-green.

The occurrence of a uranium mineral in this phosphorite shows that it is of purely inorganic origin: for uranium has never yet been found in organisms or their products of decomposition, and the supposition of a subsequent infiltration of uranium salts into the previously formed phosphorite is inconsistent with the mode of occurrence of the lime-uranite as above described. On the other hand crystalline rocks are known to contain, not only phosphoric acid, but also uranium in small quantities, as shown by the previously known occurrence of lime uranite in these rocks, and by the recently observed occurrence of uranophane in the granite of Rohrlach in Lower Silesia.

H. W.

Composition and Formation of Azurite.

By F. WIBEL (Jahrbuch für Mineralogie, 1873, 245—251).

NEARLY all the published analyses of azurite indicate a difference between the actual composition of the mineral and that which it should have in accordance with the formula—

$$Cu_3C_2O_7 + H^2O, \text{ or } 3CuO.2CO_2 + H^2O,$$

viz., 69·2 p.c. CuO, 25·6 CO_2, and 5·2 H_2O, the carbonic anhydride found being less than the calculated amount by 0·1 to 1·56 p.c., and the water in excess of the calculated quantity by 0·24 to 1·28 p.c. A specimen of massive-crystalline azurite from Siberia, freed as completely as possible from gangue and admixed malachite, carefully dried over sulphuric acid and at 100°, gave by analysis, after deduction of 4·06 p.c. insoluble admixtures (ferric oxide, silica, &c.), 69·21 p.c. CuO, 24·26 CO_2, and 6·08 water. This result, like that of all previous

analyses, indicates a composition intermediate between that of azurite and that of malachite, $2CuO.CO_2 + H_2O$ (71·9 p.c. CuO, 19·9 CO_2, 8·2 H_2O), and leads to the supposition that azurite may be formed from malachite by abstraction of water and addition of carbonic anhydride, a supposition further suggested by the fact that azurite and malachite almost invariably occur together.

That azurite may actually be formed from malachite in this manner is shown by the following experiment. Small pieces of marble were introduced, together with a moderately strong solution of cupric sulphate, into a tube of Bohemian glass, which was then sealed and heated to 150°—190° for about 24 hours. On removing the tube from the air-bath, the liquid was found to be completely decolorised, and the lumps of marble were covered with a crust of malachite of a fine green colour. This indeed is a well known result. But further, on setting the tube aside, still closed, and at the temperature of the air, small crystals of gypsum began to separate after about a week, their quantity continually increasing for several weeks more, while at the same time the liquid almost entirely disappeared, and the green crust of malachite on the marble became dotted with small dark blue nodules, which gradually increased till they formed in some parts a compact coating. On opening the tube after about three-quarters of a year, no tension was found inside. The dark blue substance was easily recognised as a copper carbonate, but no quantitative analysis was made of it, on account of the difficulty of obtaining it in sufficient quantity free from the malachite to which it adhered; but the dark blue colour and the crystalline character of the nodules* afforded sufficient proof that they consisted of azurite.

The mode of action in this experiment is easily understood. The mutual action of the calcium carbonate and copper sulphate at a high temperature produces copper carbonate (malachite), calcium sulphate and carbonic anhydride. The calcium sulphate is at first held in solution, not as gypsum but as anhydrite; otherwise it would crystallise out as gypsum either during the heating of the tube, or at all events during cooling, especially as its quantity is somewhat considerable; since, however, the actual separation of the gypsum is very gradual, we must suppose that it is slowly formed after cooling by combination of the anhydrite with water.

The first stage of the process above described may accordingly be represented by the equation,

$$2CuSO_4 + 2CaCO_3 + H_2O = \underset{\text{Malachite.}}{Cu_2CO_4.H_2O} + \underset{\text{Anhydrite.}}{2CaSO_4} + CO_2.$$

As soon as the tube cools, the anhydrite begins to be transformed into gypsum by assumption of water, which it ultimately takes from

* A similar result was obtained some years ago by Debray (*Jahresber. f. Chemie*, 1859, 211), who enclosed lumps of chalk, together with solid cupric nitrate and water, in a sealed tube, and found that, on leaving the tube to itself at the ordinary temperature, the chalk became covered with a green crust of basic cupric nitrate, on which blue crystalline nodules of azurite gradually formed. The carbonic anhydride in the tube evolved by the decomposition of the chalk exhibited a pressure of three to four atmospheres

the malachite, this latter compound at the same time absorbing carbonic anhydride which is present in a state of high tension, the final result being the conversion of the malachite into azurite—

$$3(Cu_2CO_4.H_2O) + CO_2 - H_2O = 2(Cu_3C_2O_7 + H_2O).$$
Malachite. Azurite.

This mode of formation of azurite may be thus expressed: *Azurite is formed from malachite at ordinary temperatures by addition of carbonic anhydride and abstraction of water, in presence of carbonic anhydride of high tension and a dehydrating agent.*

The assumption that native azurite is formed in this manner appears at first sight somewhat in discordance with the fact that pseudomorphs of malachite after azurite are of frequent occurrence, whereas pseudomorphs of azurite after malachite are never found. But the formation of malachite from azurite by addition of water and abstraction of carbonic acid—which undoubtedly takes place—by no means precludes the possible formation of azurite from malachite under different external conditions; and on the other hand the non-occurrence of pseudomorphs of azurite after malachite is sufficiently accounted for by the rarity of crystals of the latter mineral.

H. W.

On Maxite and Leadhillite. By H. Laspeyres (Jahrbuch für Mineralogie, 1873, 292—296).

This is a criticism of the paper by Bertrand (p. 481 of this volume) "On a new locality of Leadhillite," wherein Bertrand suggests that the hydrated sulphato-carbonate of lead from Iglesias in Sardinia, described by Laspeyres under the name of Maxite, is probably nothing but leadhillite altered by assumption of water. This view is based upon the similarity of the two minerals in their physical, and especially in their optical properties, and upon the supposed near agreement of their chemical composition.

Laspeyres, on the other hand, still maintains the existence of maxite as a distinct mineral species, and points out, in support of this view (1): That the near agreement of maxite and leadhillite in their optical properties, consisting in the fact that both these minerals have negative double refraction, and a small angle of the optic axes, which is smaller for red than for blue light ($\rho < \nu$), is quite consistent with their existence as distinct species, inasmuch as other lead-compounds are likewise optically negative (*e.g.*, cerussite and lead acetate), have $\rho < \nu$ (*e.g.*, lead acetate and anglesite), and have their optic axes inclined at a small angle (*e.g.*, cerussite). Other lead salts likewise exhibit nearly equal hardness, perfect transparency and freedom from colour, an adamantine fatty lustre on their fractured surfaces, and an adamantine nacreous lustre on their cleavage-faces of the first order. With regard to density, that of maxite, 6·87, is considerably higher than that of the Scotch leadhillite, which averages 6·35. Now Bertrand found the density of his supposed leadhillite from Iglesias to be 6·60, the determination being made upon opaque, and therefore altered specimens; he attributes the higher density to

the addition of water, and supposes that the same alteration has taken place to a greater extent in maxite. But this addition of water should rather diminish than increase the density of the mineral; and the greater density of maxite must be attributed rather to the higher proportion of sulphuric anhydride and lead oxide, and the lower proportion of carbonic anhydride which it contains.

Further the alleged near agreement of maxite and leadhillite in chemical composition is more apparent than real. Analysis gives indeed—

	PbO.	CO_2.	SO_3.	H_2O.
For Maxite	81·912	8·082	8·140	1·866
„ Leadhillite (Scotch)	80·800	11·950	7·250	—
Difference ..	+ 1·112	− 3·868	+ 0·890	− 1·866 p. c.

and these differences become still more apparent on writing the formula of maxite ($18PbO.9CO_2.5SO_3 + 5H_2O$) and that of leadhillite ($4PbO.3CO_2.1SO_3$), with equal numbers of molecules of lead oxide; they then become—

	PbO.	CO_2.	SO_3.	H_2O.
Maxite........	36	18	10	10
Leadhillite	36	27	9	—
Difference	0	− 9	+ 1	+ 10

From these differences of density and chemical composition, Laspeyres maintains the correctness of his original conclusion as to the existence of maxite as a mineral species distinct from the leadhillite of Scotland; and he infers that the so-called leadhillite from Iglesias is not a leadhillite more or less altered by hydration, but a mixture of true leadhillite with maxite.

H. W.

On the Later Montebrasite of Des Cloizeaux (Hebronite).

By F. v. Kobell (Jahrbuch für Mineralogie, 1873, 317).

The author, considering that there is some confusion in the use of the name montebrasite, now applied by Des Cloizeaux to the hydrated lithio-aluminic fluophosphate occurring at Montebras, and at Hebron in the State of Maine (see p. 793 of last volume), proposes to discard this name altogether and designate the mineral in question as Hebronite. He has examined more particularly a specimen of hebronite from Auburn in Maine. This variety colours the blowpipe strongly reddish-yellow, the red colour of the lithium being altered by the small quantity of sodium contained in the mineral. The hebronite of Auburn, and also that of Paris in Maine, exhibit a rather strong greyish phosphorescence when heated. The specific gravity of the Auburn hebronite is 3. Its analysis gave—

P_2O_5.	Al_2O_3.	Li.	Na.	F.	H_2O.	
49·00	37·00	3·44	0·79	5·50	4·50	= 100·23

agreeing with the formula—

$$3(Al_2O_3.P_2O_5) + Li_6F_6 + 2H_2O.$$

v. Kobell regards hebronite, not as an amblygonite in course of alteration, but as an independent species. The hebronite of Hebron and of Auburn is accompanied by reddish lithia-mica.

H. W.

A Cobaltiferous Magnesium Sulphate. By F. NIESS (Jahrbuch für Mineralogie, 1873, 318).

THE mineral cabinet of the University of Würzburg contains a series of minerals named "zinc-vitriol," and bearing a remarkable resemblance to sulphate of magnesium. They are aggregates of silky needles and portions of stalactites, said to have been obtained from Schemnitz and Herrengrund. The mean of several analyses of these crystals gave—

SO_3.	MgO.	CoO.	MnO.	CuO.	Water at 150°.	Remainder of the water.	
32·56	15·57	0·44	0·42	0·48	42·83	7·70	= 100

Or:

$MgSO_4$.	$CoSO_4$.	$MnSO_4$.	$CuSO_4$.	H_2O.	
46·71	0·90	0·89	0·96	50·54	= 100

The mineral from Herrengrund analysed by Niess forms stalactites about 6 centimeters long, pale red and translucent within, coated externally with a nearly white or apple-green film. The entire stalactite cleaves continuously in one direction, showing that it consists of a single individual.

H. W.

On some Belgian Minerals. By L. DE KONINCK (Jahrbuch für Mineralogie, 1873, 319).

1. BORNITE or Peacock copper-ore occurs in quartz veins in the neighbourhood of Vielm-Salm. Its analysis led to the formula Cu_5FeS_4.—2. Garnet occurs in a damourite mica-slate in the neighbourhood of Salm-Chateau. The garnets are small, usually crystallised in dodecahedrons, and are easily loosened from the rock. They belong to the modification known as *spessartin*, and contain 37 p.c. manganous oxide. This is so far remarkable in a crystallographic point of view, that the so-called spessartin has either the form 202 or 202 . ∞ O.

H. W.

Analysis of Pennine from Rympfischwäng. By P. v. HAMM (Jahrbuch für Mineralogie, 1873, 320).

THE analysis, performed in E. Ludwig's laboratory, gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MgO.	CaO.	H_2O.	
33·71	12·55	2·74	3·40	34·70	0·66	12·27	= 100·03

The chief interest of the analysis consists in the demonstration of the presence of iron in two stages of oxidation.

H. W.

Aphrosiderite. By F. NIESS (Jahrbuch für Mineralogie, 1873, 320).

THIS mineral, from the "Gelegenheit" mine near Dillenburg, was analysed in 1847 by F. Sandberger, who calculated all the iron contained in it as monoxide. A recent analysis by Niess of a specimen from Weilburg gave the result (1), which calculated to 100 parts, omitting the calcium carbonate, as an impurity, gives (2)—

	SiO_2.	Al_2O_3	Fe_2O_3.	FeO.	MgO.	CaO.	CO_2.	H_2O.	
(1.)	23·67	24·26	8·17	29·41	1·75	1·28	1·01	8·83	= 98·38
(2.)	24·63	25·25	8·50	30·61	1·82	—	—	9·19	= 100

The older analysis by Sandberger and the recent one by Niess, differ so widely that no admissible formula for the mineral can be deduced from them. The composition of other minerals designated by different authors as "aphrosiderite" or as "resembling aphrosiderite," cannot be discussed, on account of incomplete determination of the state of oxidation of the iron contained in them. Those in which the monoxide and sesquioxide were separately determined are specifically different from aphrosiderite. On the other hand, it is probable that aphrosiderite is identical with Breithaupt's thuringite.

From a recent communication by Sandberger, it appears that aphrosiderite occurs in the "All Saints" mine at Weilburg.

H. W.

The Basalts of Styria. By G. UNTCHJ (Jahrbuch für Mineralogie, 1873, 321).

NEAR the watering place of Gleichenberg, basaltic rocks rise out of the tertiary deposits. One of these basalts near Weitendorf, 2½ miles from Graz, is partially disintegrated, has a bluish-grey colour, a uniformly dense texture, and exhibits under the microscope crystals of felspar and olivine. Another basalt occurs in the miocene deposits near the village of Kloch. Here a dense basalt and basaltic tufa are found in alternate layers, while above them is a basaltic breccia consisting of fragments of a porous spongy rock, cemented by a red-brown wacke-like mass.

Of the following analyses: (1) is of the basalt of Weitendorf; (2) of the dense basalt of Kloch; (3) of the spongy porous mass (basaltic lava) of Kloch. The mean results of analysis are—

	SiO_2.	TiO_2.	P_2O_5.	Al_2O_3	Fe_2O_3	FeO.	CaO.	MgO.	K_2O.	Na_2O	H_2O.	
(1.)	54·08	1·44	trace	16·39	11·62	4·18	4·91	trace	2·31	1·96	3·61	=100·50
(2.)	42·76	1·83	0·88	11·57	16·91	3·90	2·22	2·10	3·25	10·62	4·23	=100·30
(3.)	44·15	0·84	0·83	15·41	20·85	—	4·54	8·56	0·31	4·48	—	= 99·97

The first two of these rocks are remarkable for their small amounts of lime and magnesia.

The examination of thin sections of the Weitendorf basalt shows that its mass is chiefly made up of right-angled forms of felspar crossing one another in various directions, and accompanied by crystals of

olivine and granules of magnetic iron ore, also by small brown crystals and slender needles, probably of augite. Between these felspars may be recognised, an amorphous colourless ground-mass. The olivine crystals have a deep bottle-green colour, and are very pure and fresh. This basalt may in fact be described as a felspathic basalt, having a vitreous ground-mass, and for its chief constituents one of the more siliceous felspars.

The dense basalt of Kloch differs from that of Weitendorf, not only in chemical composition, but also by its mineralogical constitution, as shown by microscopic examination, appearing as an even-grained mixture of a colourless strongly double-refracting substance, with an opaque substance enclosing numerous crystals, some of which are visible to the naked eye. These crystals exhibit under the polarising microscope the finest colours of thin plates, and a distinct polysynthetic structure in sections perpendicular to the tabular faces. Neither augite nor olivine crystals are perceptible in the granular mass, which however contains groups of slender needles, possibly of apatite.

H. W.

Occurrence of Zeolites in the Basalt of the Limperichkopf at Asbach. By A. WEISS (*Jahrbuch für Mineralogie*, 1873, 319).

THE cavities of this basalt contain phillipsite, natrolite, and apophyllite, also pectolite as a product of decomposition, and calcspar. The phillipsite is of unusual size, almost equal to that of harmotome; the apophyllite, for the most part rare in Rhenish basalts, is very clear, colourless or brownish, and has the tabular character of the Fassa valley crystals in the combination oP . P . ∞ P ∞. These minerals often occur together in the same cavity, and in that case their succession in age can be easily traced. Of the three zeolites, phillipsite is always the oldest; then follows natrolite, then apophyllite sometimes traversed by natrolite. Small brown crystals of calcspar are imbedded in the phillipsite. The course of the secondary zeolite formation may be easily traced, the cavity being in the first place lined with a zone of porous decomposed basalt, distinctly separated from the undecomposed rock. This zone of decomposition is easily seen to be connected with the secondary formation of minerals, the zeolites having plainly originated from a portion of the basaltic mass. Apophyllite, the most soluble of the zeolites, has been the last to separate in the crystalline form.

H. W.

Analysis of Eclogite from Eibiswald in Styria. By J. MAUTHNER (*Jahrbuch für Mineralogie*, 1873, 323).

THIS rock consists of a granular mixture of garnet, omphacite, hornblende, and a small quantity of quartz. The garnet encloses minerals of various kinds which are grouped round the centre of the crystals. The following analysis (the first that has been made of eclogite) is by E. Ludwig :—

SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	CaO.	Na_2O.	K_2O.	
50·13	14·37	13·02	6·46	12·85	2·35	0·14	= 99·32

H. W.

Organic Chemistry.

Methylene Acetochloride. By L. Henry
(Deut. Chem. Ges. Ber., vi, 739—744).

Chlorine was passed into cooled methyl acetate until hydrochloric acid was evolved in considerable quantity; the product now yielded a portion passing over between 100° and 120°, and this, when dried and submitted to fractionation, yielded *Methylene acetochloride*, $CH_2 \begin{cases} Cl \\ C_2H_3O_2 \end{cases}$.

Methylene acetochloride is a colourless liquid, having a penetrating and suffocating odour and a burning taste. It has a specific gravity of 1·1953, and a vapour-density of 3·70, is insoluble in water, soluble in alcohol or ether, and boils at 115°—116°. It is decomposed by water or alkalis, with formation of hydrochloric acid, acetic acid, and probably formic aldehyde. Sulphuric acid decomposes it, hydrochloric acid being evolved, and a sulpho-acid of methylene (probably $CH_2(HSO_4)_2$) being formed. When this acid is distilled with water, it appears to yield formic aldehyde or a polymeride of this substance. When methylene aceto-chloride is warmed with alcoholic potassium acetate, it yields methylene diacetate; and when it is treated with potassium sulphocyanate a violent reaction takes place, a substance which has the composition, $CH_2 \begin{cases} CNS \\ C_2H_3O_2 \end{cases}$ being probably formed. Ammonia and aniline react on methylene acetochloride, apparently forming methylene bases.

The author hopes to employ methylene acetochloride extensively in synthetical researches, and he is at present engaged in studying its action on zinc-ethyl, which should yield primary propyl alcohol.

Methyl chloracetate, $CH_3.C_2H_2ClO_2$, was obtained by passing hydrochloric acid into a solution of monochloracetic acid in methylic alcohol. It is a neutral colourless liquid having a rather agreeable odour. It boils at 126°—127°, has a specific gravity of 1·22 at 15°, and a vapour-density of 3·71. Water does not dissolve it, and it is either not decomposed by this liquid or decomposed very slowly. Aniline does not act on it at ordinary temperatures, and when it is allowed to remain for some time in contact with ammonia, it yields chloracetamide. Sulphuric acid does not cause the liberation of hydrochloric acid from it.

When methyl formate is treated with chlorine, an energetic reaction takes place, a substance boiling at about 100° being formed; this the author considers to be *methylene formochloride*, $CH_2 \begin{cases} Cl \\ CHO_2 \end{cases}$, and he considers it probable that methyl chlorocarbonate is also formed.

The author intends to study the action of chlorine on the alcohols,

acids, and ethers of the fatty series, and he considers that the action of chlorine on alcohol is not merely a dehydrogenation, but that a compound, $CH_3—CH\langle{}^{Cl}_{HO}$, is first formed, and that this splits up into aldehyde and hydrochloric acid. By treating isopropyl ether with chlorine, he hopes to obtain chlorinated derivatives of the unknown glycol, $CH_3—C(HO)_2—CH_3$.

T. B.

Preparation of Ethylene and of Ethylene Bromide. By E. ERLENMEYER and H. BUNTE (Ann. Chem. Pharm., clxviii, 64—66).

THE authors prepare ethylene by heating 25 grams of alcohol with 150 grams of sulphuric acid, a mixture of equal parts of alcohol and sulphuric acid being gradually added as soon as the action slackens. Ethylene bromide was prepared by passing the gas through a long inclined tube half filled with bromine and kept cool. By operating as described, it is easy to prepare 1000—1100 grams of the bromide in seven hours.

T. B.

Production of Methyl Alcohol by the Distillation of Dry Calcium Formate. By C. FRIEDEL and R. D. SILVA (Compt. rend., lxxvi, 1545).

THE authors point out that previous to the paper by Lieben and Paterno (*Ann. Chem. u. Pharm.*, cxlvii, 298), they had announced the same results (*Bull. Soc. Chim.* [2], xix, 481). In this paper they give full details of their mode of proceeding.

B. J. G.

Derivatives of Normal Propyl Alcohol. By H. ROEMER (Deut. Chem. Ges. Ber., vi, 784—786).

Normal propyl mercaptan was obtained by digesting normal propyl bromide with an alcoholic solution of potassium sulphydrate, distilling the product, and adding water to the distillate. Under these circumstances the mercaptan is precipitated as a colourless mobile fluid, having the odour which is characteristic of mercaptans. It boils at 67°—68°, is not quite insoluble in water, and it unites with freshly precipitated mercuric oxide, forming the mercaptide $(C_3H_7S)_2Hg$, which crystallises in shining leaflets melting at 68°.

Normal Propyl-disulphocarbonic Acid.—The potassium salt of this acid was obtained in shining yellow needles by adding carbon disulphide to a solution of potassium hydrate in normal propyl alcohol, and crystallising the yellowish mass which is deposited. The addition of an acid to the potassium salt causes the separation of free propyl disulpho-

carbonic acid in the form of an oil, which soon undergoes decomposition.

Tripropyl Biuret.—Attempts to prepare normal propyl cyanate by the action of the iodide or bromide on silver cyanate were unsuccessful, but when a mixture of potassium propylsulphate and potassium cyanate was distilled, propylene was given off and a yellowish solid distillate was obtained, which, after crystallisation from alcohol, was found to be *tripropyl biuret*, $CON_2(C_3H_7)_3CONH_2$.

Tetrapropylammonium Iodide and Tetrapropylammonium Hydrate.—By digesting normal propyl iodide with alcoholic ammonia, again treating the mixed bases so formed with propyl iodide, distilling off the excess of propyl iodide, and adding soda to a solution of the product, *tetrapropylammonium iodide* was separated in the solid state. It crystallises in beautiful white prisms. The iodine in this compound was replaced by chlorine when it was digested with silver chloride, and on adding platinum chloride, a red crystalline salt was deposited having the composition $[(C_3H_7)_4NCl]_2PtCl_4$. When tetrapropylammonium iodide is treated with silver hydrate, the base $(C_3H_7)_4N.OH$ is liberated. It forms a deliquescent mass which absorbs carbonic acid from the air. It is not decomposed at 100°, but at a higher temperature it is decomposed into propylene, tripropylamine, and ammonia.

The platinum salt of tripropylamine crystallises in brick-red leaflets, less soluble in water than in alcohol or ether.

The author intends to study the properties of free tripropylamine, propylic mustard oil, and other derivatives of normal propyl alcohol.

T. B.

Preparation of Trimethyl Carbinol. By A. Butlerow (Ann. Chem. Pharm., clxviii, 143—144).

This body is, according to Linnemann, conveniently prepared by the action of isobutyl iodide and acetic acid on silver oxide. But by following strictly Linnemann's directions, as well as by changing the conditions, Butlerow always obtained a mixture of trimethyl carbinol and isobutyl alcohol.

C. S.

Formation of Glycerin from Propylene. By C. Friedel and R. D. Silva (Compt. rend., lxxvi, 1594—1598).

To remove the objection urged by Berthelot against their synthesis of glycerin (this Journal [2], x, 399), that the propylene employed being prepared from allyl iodide was itself derived from glycerin, the authors have repeated their experiments with propylene prepared by dehydration of isopropyl alcohol, of which they had obtained a considerable quantity, as by-product, in the preparation of pinacone from acetone. The results obtained are entirely confirmatory of those previously published, and thus establish beyond doubt that it is possible to synthesize glycerin from its elements.

In the preparation of propylene from isopropyl alcohol, the authors recommend the use of fused zinc chloride as dehydrating agent, the

mixture of alcohol with (about 2·5 times (?) its weight of) the chloride being left to itself 24 hours and then heated on a sand-bath, when a regular evolution of gas takes place. The gas is in great part absorbed by a concentrated aqueous solution of iodine chloride, with production of propylene iodochloride, of which a fair yield is obtained; thus 250 grams alcohol and 650 grams zinc chloride gave 250 grams propylene iodochloride. To convert the iodo-chloride into propylene chloride it was acted upon by chlorine in presence of water, the passage of the gas being continued until the separated iodine was redissolved as iodine chloride; it appears that in this way mere traces only of more highly chlorinated products are formed. The purified propylene chloride was next heated with dry iodine chloride in sealed tubes to 140°; after 8 hours' digestion the tubes were opened and the hydrochloric acid allowed to escape, then closed and again heated for eight hours. The separated iodine was removed by passing chlorine through the tube-contents mixed with water until solution was effected; the oil was then decanted, and, after drying, submitted to fractional distillation and split up into a number of fractions weighing together 146 grams, of which only 18·8 grams boiled at 150°—160°. Analysis shewed that probably nearly one-half of this impure trichlorhydrin consisted of tetrachloropropane, but as this in no way interferes with the conversion of trichlorhydrin into glycerin by Berthelot's method, the mixture in portions of 2·5 grams was enclosed in tubes with about 45 grams of water and heated to 180° during a night. By appropriate treatment the authors were able to separate a small quantity of glycerin from the product of the action of water, and to characterise it by the formation of acrolein and allyl iodide.

H. E. A.

Preparation of Dichlorhydrin. By A. Claus (Ann. Chem. Pharm., clx, 42—44).

Dichlorhydrin is most conveniently prepared by using Carius's method and proceeding as follows:—Glycerin is concentrated till it boils at 195°; 800 grams are placed in a flask connected with a reversed condenser, and two kilograms of sulphur chloride, S_2Cl_2, are gradually added, the mixture being well shaken and heated in a salt-bath. After seven or eight hours, the condenser is removed and the product heated an hour longer to expel sulphur dioxide and hydrochloric acid. The cooled mass is exhausted with ether, the solution first distilled in a water-bath, and the residue distilled over the naked flame. Dichlorhydrin is formed according to the equation—

$$C_3H_8O_3 + 2S_2Cl_2 = C_3H_6Cl_2O + SO_2 + 2HCl + 3S.$$

800 grams of glycerin yielded 700 grams of pure dichlorhydrin, boiling at 178°. The by-products consist of higher-boiling bodies containing sulphur.

C. S.

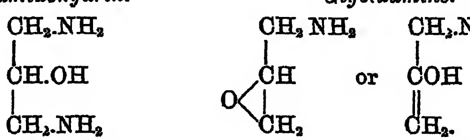
Action of Ammonia on Dichlorhydrin. By A. CLAUS (Ann. Chem. Pharm., clxviii, 29—42).

WHEN dichlorhydrin is heated with alcoholic ammonia to 105°, it yields ammonium chloride and *chlorhydrinimide*, $C_{12}H_{27}N_3Cl_2O_4$, which is a white amorphous mass, insoluble in water, alcohol, ether, and concentrated acids, and not acted upon even by boiling it with sulphuric acid, aqua regia, or concentrated potash. In hot water it swells up enormously and yields a perfectly transparent jelly. It seems to be identical with the compound which Reboul obtained by the action of alcoholic ammonia on epichlorhydrin. By heating it with slaked lime to a red heat it yields an oily distillate containing a resin and basic compounds. Quantitative experiments showed that chlorhydrinimide is formed in the calculated quantity, only when for 4 mol. of dichlorhydrin 9 mol. of ammonia are employed and the alcohol contains about 4 per cent. of the latter. By using a solution containing only about 1 per cent. two new bases diamidohydrin and glycidiamine are formed, but no chlorhydrinimide.

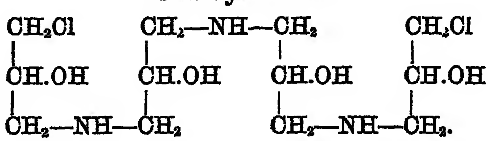
Diamidohydrin hydrochloride, $C_3H_{10}N_2O.2HCl$, is a very hygroscopic substance and is partially decomposed, with formation of ammonium chloride, when its alcoholic solution is evaporated. The platinochloride is also easily decomposed by water; it forms transparent prisms or needles, having the composition $C_3H_{10}N_2O.2HCl + PtCl_4$

Glycidamine hydrochloride, $C_3H_7NO.HCl$, is obtained in crystals by precipitating its alcoholic solution with ether; it is also very hygroscopic, but appears to be more stable than the preceding compound. The platinum salt, $2(C_3H_7NO.HCl) + PtCl_4$, crystallises in transparent glistening needles. Glycidamine appears to be identical with Berthelot's and Luca's *glyceramine*. The constitution of these bases is explained by the following formula:—

Diamidohydrin. *Glycidamine.*



Chlorhydrinimide.



C. S.

Di-iodhydrin. By A. CLAUS (Ann. Ch. Pharm., clxviii, 21—29).

Di-iodhydrin, $C_3H_6I_2O$, is obtained by heating dichlorhydrin with water and potassium iodide in sealed tubes not above 110°; the crude product

is purified by shaking it with a solution of hydrogen sulphide and filtering the oil through asbestos to remove free sulphur. It is a thick yellowish liquid having the specific gravity of 2·4 at 15°, and solidifying at − 16°—20° to a crystalline mass. On heating it to 70°—76° it gives off iodine and the smell of acrolein, and when more strongly heated, water and a brown, oily liquid containing some di-iodhydrin and other products distil over.

C. S.

Oxalin. By Lorin (Compt. rend., lxxvii, 129).

A mixture of oxalic acid and glycerin gives rise to a white, silky, deliquescent body, for which the name *oxalin* is proposed. It is converted into oxamide by ammonia, and by oxalic acid into a substance resembling mannite.

B. J. G.

Diallyl and Attempts to obtain Allyl-benzene. By Wagner and Tollens (Deut. Chem. Ges. Ber., vi, 588—593).

When 48 parts of allyl bromide, 56 of brombenzene, 102 of benzene, and 23 of sodium are heated together to 60°, an energetic action commences, which must be moderated by cooling. On distillation over a naked flame, a distillate was obtained consisting principally of benzene and diallyl, a carbonised residue remaining behind. In another instance the distillation was effected in the water-bath, and the residue was treated with alcohol; the addition of water now caused the separation of an oily substance, which, on distillation in a current of steam, yielded a small proportion of a distillate containing diallyl but no allylbenzene, and a thick residue smelling of styrol, which deposited crystals apparently consisting of diphenyl.

The authors consider it probable that allylbenzene is formed and that the products of its polymerisation are contained in the thick oil just mentioned. This oil combines with bromine, no hydrobromic acid being evolved.

The diallyl tetrabromide obtained from the diallyl formed during the above reaction was, after purification, found to melt at 62·5°—63·5°, although 37° is the melting point usually attributed to this substance. In order to arrive at a solution of this difference, diallyl was prepared by the action of sodium on a mixture of allyl bromide and benzene, to which a small quantity of alcohol had been added, also by the method of Oppenheim, and by the action of silver on allyl bromide. Diallyl from these sources was found to boil at 58°—60°, and its tetrabromide, when pure, melted between 60° and 63·5°.

The boiling point of diallyl appears to indicate that it is rather analogous in structure to the di-isopropyl investigated by Silva and by Schorlemmer, than to the normal dipropyl.

T. B.

Action of Hypochlorous Acid on Allyl Chloride.
By H. von Gegerfelt (Deut. Chem. Ges. Ber., vi, 720—721).

The author has previously found that by combining allyl chloride with hypochlorous acid, a chlorhydrate is obtained, which is isomeric with dichlorhydrin, while, according to Henry, the two compounds are identical. He has now repeated his experiments on a larger scale, and found that the chief product boiled as before at 183°; concentrated potash converts it into epichlorhydrin, boiling at 117°, and this combines with hydrochloric acid and yields common dichlorhydrin, boiling at 176°—177°.

C. S.

Propargyl Compounds. By L. Henry (Deut. Chem. Ges. Ber., vi, 728—730).

Propargyl alcohol is obtained, together with *monobromallyl oxide*, by the action of potash on monobromallyl alcohol. The pure alcohol boils at 114°—115°; it cannot be dehydrated with anhydrous baryta, because it combines with it, forming the compound $(HO.C_3H_2)_2Ba + C_3H_3.OH$, crystallising in small plates. By acting with hydrochloric acid on the alcohol, no propargyl chloride is formed, but an additive product.

Propargyl bromide, C_3H_3Br, is formed, together with $C_3H_4Br_2$, by treating the alcohol with phosphorous bromide; it boils at 88°—90°, and has at 20° the specific gravity 1·52.

Propargyl iodide is produced by the action of iodine and red phosphorus on the alcohol; it boils at about 120°, but decomposes at the same time.

Propargyl acetate is readily obtained by acting on the alcohol with acetyl chloride. It boils at 124°—125°, and has the specific gravity 1·0031 at 12°; its smell is not agreeable.

Propargyl sulphocyanate, C_3H_3SCN, is easily produced by the action of the bromide on an alcoholic solution of potassium sulphocyanate. It is an oily liquid, smelling like mustard-oil, and is decomposed by heat.

Monobromallyl oxide, $(C_3H_4Br)_2O$, is a liquid boiling at 212°—215°, and possessing a faint smell. Its specific gravity is 1·7 at 17°.

Whilst, as Tollens has shown, the allyl compounds boil at the same temperature as the corresponding primary propyl compounds, the propargyl compounds boil 18°—20° higher than the allyl compounds.

C. S.

Mannite and its Derivatives. (Continuation: see this Journal [2], x, 70; xi, 160, 747.) By G. Bouchardat (Compt. rend., lxxvi, 1550—1554).

The author has examined mannite and some of its derivatives afresh, using the polariscope of Jelett and Cornu. Mannite did not deviate the plane so much as 0° 2′, which is the smallest amount capable of being measured by this the most perfect polariscope known. The first column of figures in the following table gives the new observations of

the *specific* rotatory power of the substances named. The second column gives the (calculated) *molecular* rotatory power for the same weight of mannite in each form.

	I.	II.
Dichloromannite	− 3·7°	− 4·5°
α Mannitan	+ 6·8°	+ 6·1°
β Mannitan	+ 10·4°	+ 9·3°
Monochloromannitan	+ 18·7°	+ 18·7°
Monobromomannitan	+ 22·0°	+ 27·4°
Diacetomannitan	+ 22·6°	+ 30·8°
Tetracetomannitan	+ 23·0°	+ 41·9°
Hexacetomannite............	+ 18·0°	+ 42·9°
Hexnitromannite............	+ 42·2°	+ 104·8°
Nitromannitan..............	+ 27·2°	x

The following fresh observations have also been made. *Hexacetomannite* crystallises from acetic anhydride in symmetrical orthorhombic crystals, melting at 119°. The following angle measurements were made:—

$m : m = 73° 40'$, $a^2 : p = 140° 42'$, $e^1 : p = 114° 50'$, $m : a^2 = 112° 2'$.

Tetracetomannitan, $C_6H_8O.(OC_2H_3O)_4$, is formed by the prolonged action of a large excess of acetic anhydride on mannite. It is not crystallisable. *Dichloromannite* crystallises from water in clinorhombic forms, with cleavage plane parallel to p, and plane of optic axes parallel to g. The angles observed were:—

$m : m = 91° 23'$, $m : g = 133° 14'$, $m : p = 91° 50'$, $p : b^1 = 118° 16'$.

(Several statements in this paper are contradictory to, or greatly modify, statements made in former papers, *e.g.*, monochloromannitan is said (p. 748 of this volume), to have a rotatory power of +6 99; hexacetomannite is said (p. 70, last volume), to have no action on polarised light, and to melt at 100°; diacetomannitan, $C_6H_8O.(OC_2H_3O)_2.(OH)_2$, is evidently the body to which the formula, $C_6H_{10}(C_2H_3O)_2O_4$, is given on p. 70, last volume.)

B. J. G.

On the Presence of Arabic Acid in the Sugar-Beet, and on Arabin Sugar. By C. Scheibler (Deut. Chem. Ges. Ber., vi, 612—622).

The author describes the further examination of a constituent of the cellular tissue of the sugar-beet, which, under certain circumstances, passes over into the juice and then most seriously hinders the extraction of crystalline sugar, to which he first drew attention now five years ago (*Deut. Chem. Ges. Ber.*, i, 58 and 108). This substance was originally examined by Fremy, who, on account of its supposed identity with an acid obtained from pectin, termed it metapectic acid. Its complete investigation has been much delayed, on the one hand by the circumstance that it is not always obtainable in sufficient quantity from the beet, the harvest of 1868–69 having furnished scarcely any, whereas

that of 1872–73 yielded a large quantity; on the other, by the extreme difficulty of rendering it pure. A number of analyses of products obtained from beet grown in various years, when allowance is made for the ash left on combustion, give concordant numbers which lead to the formula, $C_{12}H_{22}O_{11}$. This formula, however, is the same as that assigned to arabin or arabic acid (from gum arabic); and a comparison of the properties of the two substances shows that they are in all probability identical, which is rendered certain by the fact that when acted upon by dilute sulphuric acid, each yields a sugar, $C_6H_{12}O_6$, that obtained from the so-called metapectic acid exhibiting precisely the same crystalline form, optical rotatory power, and other properties as that obtained from arabin. This sugar, on account of its formation from arabin, the author terms *arabinose;* it crystallises in well-formed rhombic prisms (measurements of the angles by Prof. Groth are given); the rotatory power of the freshly-prepared solution is $[\alpha] = +121$, which becomes $+116$ after the solution has been prepared for some time, and after warming; arabinose is not fermentable. It is probable that under normal conditions arabin is present in ripe healthy beet, either entirely or in great part in the insoluble state, as so-called *metarabic acid* (*metarabin*).

In his first communication the author stated that sugar-beet arabin was strongly lævorotatory: $[\alpha] = -98{\cdot}5$. According to Béchamp gum arabic is also lævorotatory: $[\alpha] = -36$. The first sample examined by the author proved to be dextrorotatory, which led him to examine other samples procured from a trustworthy source; and he found that the rotatory power varied from sample to sample, some being more or less lævorotatory, others more or less dextrorotatory; the amount of crystalline sugar furnished by different samples on inversion also differed. Moreover, both sugar-beet arabin and gum arabic always gave, together with arabinose, a certain quantity of a non-crystalline, apparently fermentable sugar, of which considerably less was obtained from the former than from the latter, a fact which is in evident relation to the circumstance that sugar-beet arabin has a more pronounced lævorotatory action than any of the lævorotatory samples of gum arabic examined. Hence it appears that whilst sugar-beet arabin consists of a powerfully lævorotatory substance (which is usually the main constituent), yielding arabinose, and a second closely allied substance which yields a non-crystalline sugar on inversion—gum arabic, as a rule, contains proportionately more of the latter and less of the former constituent. This view is strengthened, and the analogy between the arabins from the two sources rendered still closer, by the fact that, in preparing arabin from beet from various sources during the past season, the author has observed that in a few cases the product had a slight dextrorotatory action.

The method which the author employs in extracting arabin from sugar-beet is as follows:—The fresh pulp is freed as much as possible from the juice by pressure; the pressed cake is broken up and macerated for several hours with alcohol of 86—90 per cent. Tralles; the alcohol is then poured off, and that which is absorbed removed by pressing, and the pressed cake again submitted to similar treatment. By this means the cane-sugar and most of the non-saccharine substances are removed without the metarabin of the cellular tissue being rendered soluble.

The pressed mass is now introduced into boiling water, and heated for some time; pure milk of lime is then added until the solution is strongly alkaline; and the whole is warmed on the water-bath. The metarabin is thus rendered soluble. The solution containing the calcium derivative of arabin is then separated and treated with carbonic anhydride to remove the excess of lime, filtered, concentrated to a small volume on the water-bath, again filtered, rendered strongly acid by the addition of acetic acid, and mixed with a large excess of alcohol; the impure gum is thus precipitated as a glutinous ropy mass. After some time the alcohol is poured off, the gum dissolved in a small quantity of water and reprecipitated by alcohol, this treatment being then several times repeated. After a time the arabin is precipitated in flocculi, but however often the dissolution and reprecipitation be repeated, it is impossible to obtain the arabin free from ash constituents.

In conclusion, the author describes a gum different from the above, produced in the fermentation of beet-juice. The juice, when left to itself, assumes after a time a gummy consistency, but on further standing again becomes liquid, and enters into more or less rapid fermentation; the gas at first evolved contains about 15 per cent. of hydrogen, but finally carbonic anhydride alone is evolved. At the conclusion of the fermentation, the solution contains a gum which may be precipitated by alcohol, mannite, a liquid sugar, lactic acid, &c. The gum, which is dextrorotatory, has the same composition as arabin, but on inversion by dilute sulphuric acid, it yields a sugar which remains liquid, and is further distinguished from arabin by yielding a blue flocculent precipitate with Fehling's solution.

H. E. A.

Pivalic Acid. A New Isomeride of Valeric Acid.

By C. FRIEDEL and R. D. SILVA (Compt. rend, lxxvii, 48—52).

PINACOLINE oxidised with a mixture of sulphuric acid and potassium dichromate, furnishes a new volatile and crystallisable acid which is isomeric with valeric acid. The authors name this compound pivalic acid. Purified by fractional distillation and fusion, it boils at 163° and crystallises at 30°. Special attention was paid to these determinations in consequence of the great resemblance between pivalic acid and the trimethacetic acid of Butlerow.

That chemist found the melting point of his acid to be 34° to 35°, and boiling point 161°. He has also described a barium salt which crystallises in fine needles grouped in stars, containing $(C_5H_9O_2)_2Ba.5H_2O$.

Pivalate of barium contains the same quantity of water. The identity of the two acids seems therefore not improbable. Pivalic acid, however, is always obtained in the crystalline, never in the vitreous state, as trimethacetic acid partly presents itself. The crystals are small octohedrons of the regular system, and are grouped together in dendritic or granular masses. The acid is soluble in 46 times its weight of water at 20°.

The silver salt is obtained in small crystalline laminæ when a pivalate is precipitated by nitrate of silver.

The sodium salt crystallises with two molecules of water, which it loses in dry air. The potassium salt is deliquescent.

These salts are easily decomposed by acetic acid, with liberation of pivalic acid.

Pivalate of copper is almost insoluble in water, and is readily converted into a basic salt by treatment with a large quantity of water. It is soluble, however, in alcohol, from which it crystallises in beautiful bluish-green prisms, which contain both alcohol and water of crystallisation, probably $(C_5H_9O_2)Cu.H_2O.\frac{1}{2}C_2H_6O$. On exposing the salt to the air, the alcohol evaporates away rapidly.

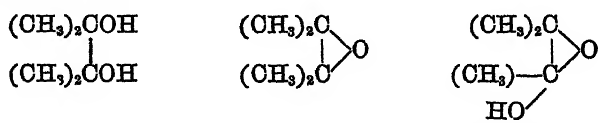
The copper salts when heated present a curious phenomenon. A white fume disengages itself from the gently heated salt, condensing again upon the surface in the form of a fibrous non-crystalline mass resembling cotton. These fibres are not volatile; they consist of a copper salt which is capable of dissolving in ammonia, forming a solution which at first is colourless.

Barium and calcium pivalates are very soluble in water. They contain respectively five and four molecules of water of crystallisation.

By the action of ethyl iodide upon sodium pivalate, *ethyl pivalate* has been obtained as a limpid liquid of agreeable odour, boiling at 118·5°, and containing $C_5H_9O_2.C_2H_5$. Its specific gravity is ·8773 at 0°, and ·8535 at 25°.

The distillation of calcium pivalate with formate, gave a small quantity of a liquid of aldehydic odour, boiling about 90°, and regenerating pivalic acid by oxidation.

If it should ultimately be shown that pivalic and trimethacetic acids are not identical, the former must be represented by the third of the following formulæ:—



Pinacone. Pinacoline. Pivalic acid.

This formula, it will be observed, does not contain the group CO_2H, which has been hitherto regarded as characteristic of the acid function.

W. A. T.

Transformation of Succinic into Maleic Acid.

By E. BOURGOIN (Compt. rend., lxxii, 52).

WHEN succinate of silver mixed with sand is heated to a temperature somewhat above 100°, part of it is resolved into metallic silver and maleic acid:

$$C_4H_4Ag_2O_4 = Ag_2 + C_4H_4O_4.$$

A small quantity of succinic acid is at the same time regenerated, whilst a carbonaceous residue is left.

W. A. T.

Pyroracemic Acid. By B. BÖTTINGER (Deut. Chem. Ges. Ber., vi, 787—790).

AMONG the products of the action of barium hydrate on pyroracemic acid, the author found, besides uvitic acid, a certain proportion of acetic acid and of oxalic acid, but he did not succeed in isolating Finkh's uvitonic acid.

When pyroracemic acid is heated with water to 130°, a small quantity of carbonic anhydride is evolved, this being probably due to the formation of a trace of pyrotartaric acid, but the bulk of the pyroracemic acid remains unchanged. When, however, the heat is raised to 160°, a considerable quantity of carbonic anhydride is evolved, and products not yet investigated are formed.

The author considers that the formula

$$\begin{array}{l} CH_2 \diagdown \\ | \qquad \rangle O \\ CH \diagup \\ | \\ COOH \end{array}$$

, explains the metamorphoses of pyroracemic acid better than that at present employed; but if glyceric acid should be formed by addition of the elements of water to pyroracemic acid, decisive evidence will be obtained in favour of the proposed formula.

When pyroracemic acid is warmed with concentrated nitric acid, an action takes place, resulting in the formation of oxalic acid, together with traces of formic acid and a small quantity of carbonic acid. Barium peroxide acts violently on pyroracemic acid, a barium salt being formed, which gives numbers indicating its correspondence with an acid having the composition $C_9H_{10}O_8$, this acid being probably formed thus:—

$$(C_3H_4O_3)_3 - H_2O = C_9H_{10}O_8.$$

T. B.

Chlorinated Acetonitriles. By L. BISSCHOPINCK (Deut. Chem. Ges. Ber., vi, 731—734).

CHLORINATED acetonitriles were prepared by distilling the corresponding chlorinated acetamides with phosphoric anhydride, the products being freed from acid by means of potassium carbonate, and finally distilled. They form colourless pungent liquids, insoluble in water, but soluble in alcohol or ether. Treatment with warm dilute mineral acids causes the liberation of ammonia and the formation of the corresponding acids. The chlorinated acetonitriles unite with hydrobromic acid to form crystalline compounds, which are insoluble in ether, but decomposed by water.

Monochloracetonitrile, $CH_2Cl.CN$; boils at 123°—124°, has a specific gravity of 1·204 at 11·2°, and a vapour density of 2·62.

Dichloracetonitrile, $CHCl_2.CN$; boils at 112°—113°, and has a density of 1·374 when in the fluid state, and of 3·82 when in the state of vapour.

Trichloracetonitrile, $CCl_3.CN$, boils at 83°—84° (81° Dumas and Leblanc). Its specific gravity was found to be 1·439, and its vapour-

density 5·03. It is remarkable that the trichloro-derivative boils at a lower temperature than the monochloro- or dichloro-derivative, and that the dichloro-derivative boils at a lower temperature than the monochloro-derivative. When trichloracetonitrile is heated to 100° with alcoholic ammonia, no ammonium chloride or cyanogen is formed, but merely trichlor-acetamide.

Chlorinated acetamides.—These substances were prepared by allowing the ethylic ether of the corresponding chlorinated acetic acid to remain for some days in contact with aqueous ammonia. The amides thus produced are but slightly soluble in water, the solubility diminishing as the degree of chlorination becomes greater. *Monochloracetamide* melts at 116°, and when subjected to a pressure of 743 mm., boils with partial decomposition at 224°—225°. *Dichloracetamide* melts at 96°, and under a pressure of 745 mm. distils without change at 233°—234°. *Trichloracetamide* melts at 136° and boils at 238°—239°, when the pressure is 476 mm.

T. B.

Remarks, in connection with the above Investigation, on the Volatility of the Cyanides of Negative Radicals. By L. Henry (Deut. Chem. Ges. Ber, vi, 734—737).

It is well known that when the hydrogen-atoms of an organic body are successively replaced by chlorine, the boiling point becomes higher as the proportion of chlorine becomes greater. This law obtains most completely when the group CH_3 (or C_nX_x), in which the substitution takes place, is united with another hydrocarbon group; but when the group CH_3 (or C_nX_x) is united with a negative group or negative radical, it may be noticed that there is a very considerable difference between the boiling point of the original compound and that of the monochloro-derivative, while the differences between the boiling points of the monochloro- and dichloro-derivatives and between those of the dichloro- and trichloro-derivatives are comparatively small. It may be observed that the presence of a negative radical in a compound containing cyanogen considerably increases its volatility; *e.g.*, H.CN boils at +26°, while Cl.CN boils at +15°, and CN.CN at −21°.

The fact of dichloracetonitrile and trichloracetonitrile boiling at a lower temperature than monochloracetonitrile can now be explained by assuming that the positive radical, CH_3, becomes negative when two or three atoms of its hydrogen are replaced by chlorine.

The author considers that the cyanides of negative radicals containing carbon are comparable with secondary compounds, while the true nitriles show considerable analogy to primary compounds.

T. B.

Taurocarbamic Acid.

By H. Salkowski (Deut. Chem. Ges. Ber., vi., 744—746).

The author has already shown that when taurin is administered to the human subject a portion passes unaltered into the urine. He now finds that the greater part of the taurin becomes transformed into an

acid containing the elements of 1 molecule of taurin and 1 molecule of carbamic acid minus 1 molecule of water.

The new acid, *tauro-carbamic acid*, $C_3H_8N_2SO_4$, is obtained by precipitating the urine with acetate of lead, removing the lead from the liquor by hydrosulphuric acid, evaporating the filtrate, and adding alcohol to the concentrated solution. The crude sodium salt which then separates must be treated with animal charcoal and afterwards decomposed by sulphuric acid. The crude acid may now be extracted by alcohol, which leaves it, on evaporation, in the form of a syrup which must be freed from sulphuric acid by means of barium hydrate, and from chlorine by means of silver carbonate.

Tauro-carbamic acid, when pure, forms anhydrous square leaflets, which are slightly hygroscopic in moist air. It is readily soluble in water, slightly soluble in alcohol, and insoluble in ether. When heated to 130°—140° with barium hydrate and water, it splits up into carbonic acid, ammonia, and taurin,—

$$\begin{array}{l} CH_2 - NH_2 \\ | \\ CH.SO_3H + BaH_2O_2 = C_2H_7NSO_3 + BaCO_3 + NH_3. \\ | \\ C = O.NH_3. \end{array}$$

The *barium salt* forms anhydrous shining rhombic tables; the *silver salt*, tufts of long radiated crystals.

The researches of Schültzen render it probable that tauro-sulphamic acid is also excreted in the urine when taurin is exhibited, and the author finds that normal urine contains a trace of tauro-carbamic acid.

T. B.

Sulpho-urea. By NENCKI (Deut. Chem. Ges. Ber., vi, 598—600).

WHEN a cold, saturated, aqueous solution of sulpho-urea is treated with a solution of mercury cyanide, a crystalline precipitate having the composition $CSN_2H_4 . Hg(CN)_2$ is formed. It is slightly soluble in cold water, and when the solution is boiled, it is decomposed as follows:—

$$CSN_2H_4.C_2N_2Hg = CN.NH_2 + 2(HCN) + HgS.$$

The cyanamide first formed undergoes polymerisation and becomes converted into Hofmann's dicyanamide.

A solution of sulpho-urea in warm acetic anhydride solidified on cooling to a crystalline mass, which, after crystallisation from water, gave numbers agreeing with *acetyl-sulphocarbamide*, $CS(C_2H_3O)H_3N_2$. This substance is easily soluble in alcohol or hot water and slightly soluble in cold water or ether. It is neutral, melts at 11·5° uncor. (misprint for 115° ?), and when heated with phosphoric anhydride it yields a pungent oil heavier than water. A crystalline and slightly soluble platinum salt, having the composition $CS(C_2H_3O)H_3N_2.2HCl.PtCl_4$, was obtained.

The author has prepared chloracetyl-sulphocarbamide, but on seeing the recent description of the substance by Maly and Volhard he ceased investigating it.

T. B.

Sulpho-urea. By A. Claus (Deut. Chem. Ges. Ber., vi, 726—728).

This compound is readily obtained by dissolving carbon sulphide in alcoholic ammonia and evaporating the liquid so far that ammonium sulphocyanate would crystallise out on cooling. It is then heated in a small basin over the naked flame until it froths up and white fumes are evolved; the lamp is now removed and cold water poured on the hot mass as long as effervescence takes place; on cooling impure sulpho-urea crystallises out, which is washed with cold alcohol and crystallised from water. The mother-liquor containing ammonium sulphocyanate yields more sulpho-urea by boiling it rapidly down.

When pure ethyl nitrate is added to pure sulpho-urea a solution is obtained, giving with ferric chloride the reaction of sulphocyanates; torrents of nitrogen and nitric oxide are given off, and a yellowish red body, having the properties of pseudo-sulphocyanogen is left behind. Ethyl nitrate containing nitric acid acts quite differently, the sulpho-urea being simply converted into its nitrate.

By heating sulpho-urea above the melting point, but not to dryness, compounds standing between sulpho-urea and mellam are produced, three of which have been isolated: 1. $(CN)_3(NH_2)_2SH$, not freely soluble in hot and cold water and forming yellow warty crystals. 2. $(CN)_3(NH_2)_2NH(CN)_3(NH_2)S$, freely soluble in boiling water; on cooling the solution solidifies to a jelly. 3. $(CN)_3(NH_2)_2NH(CN)_3(NH_2)NH(CN)_3(NH_2)SH$ more soluble in cold water than No. 2 and crystalline.

The three compounds have a weak acid reaction and dissolve in potash; on boiling them with dilute hydrochloric acid, they lose hydrogen sulphide and yield chlorinated products. Nos. 2 and 3 give with ferric chloride the reaction of sulphocyanates, and with lead acetate white precipitates, which are sparingly soluble in cold and freely in hot water.

C. S.

Sulphohydantoïn or Glycolyl Sulpho-urea. By R. Maly (Ann. Chem. Pharm., clxvii, 133—142).

The author confirms Volhard's statement that the product of the action of monochloracetic acid on sulphocarbamide consists of the hydrochloride of sulphohydantoin, and is not monochloracetyl-urea. It forms white crystals, which readily dissolve in water, sparingly in alcohol, and scarcely in ether. On adding ammonia or baryta-water to its warm aqueous solution, sulphohydantoïn soon crystallises out in thin, glistening prisms. It is scarcely soluble in cold water, alcohol, and ether.

C. S.

Benzoyl-sulpho-urea. By W. H. PIKE (Deut. Chem. Ges. Ber., vi, 755).

THIS body is obtained by gently heating sulpho-urea with benzoyl chloride. The product of the reaction, crystallised from alcohol, furnishes sparkling colourless needles, melting at 169°—170° (uncorrected).

Benzoyl-sulpho-urea, C_6H_5 CO NH.CS NH_2, has an extremely bitter taste, and forms an insoluble crystalline platinum salt. It is but slightly soluble in water.

By removing the sulphur by the action of lead oxide, the author hopes to obtain benzoyl-guanidine and benzoyl-dicyanamide. By this reaction he has already succeeded in producing a substance which gives a well-crystallised hydrochloride and platinum salt.

W. A. T.

Constitution of Benzene-derivatives. By THEODOR PETERSEN (Deut. Chem. Ges. Ber., vi, 368—379).

THE greater part of this paper is devoted to a discussion of the author's views on the constitution of the isomeric di-derivatives of benzene.

He notes that all attempts on his part to prepare dichlorobenzene from dichlorobenzoic acid have been unsuccessful, but that he has obtained pyrocatechin on fusion of the chlorophenol prepared from volatile mononitrophenol with potassium hydrate, a result which is confirmatory of Faust and Müller's observations (this Journal [2], xi, 633); the yield, however, appears to be extremely small. The author then refers to Armstrong's recognition of the identity of the dinitrochlorophenol obtained by Griess on nitration of crude chlorophenol with Faust and Saame's dinitrochlorophenol melting at 111° (*chloro-α-dinitrophenol*), and of the existence, as a distinct modification, of the chlorodinitrophenol (said to melt at 103°), which Stenhouse obtained by the action of iodine chloride on trinitrophenol. Armstrong's conclusions on this point, however, the author believes to be incorrect. He has examined the action of iodine chloride on trinitrophenol, and has obtained, as main product, chloro-α-dinitrophenol (m.p. 111°), together with a relatively very small quantity of the isomeride melting at 81°. He then calls attention to the circumstance that the chlorodinitrophenol melting at 69°, and the nitrodichlorophenol melting at 106°, previously described by himself (this Journal [2], ix, 246), as new compounds, are not so, but are identical respectively with Dubois' chlorodinitrophenol (m.p. 81°), and Fischer's nitrodichlorophenol (m.p. 122°), the differences in melting point and outward appearance of the metallic derivatives which originally led him to regard them as distinct modifications, having disappeared after repeated recrystallisation. Presumably also the chlorodinitrophenol (m.p. 70°) described by Engelhardt and Latschinoff, was Dubois' chlorodinitrophenol in an impure state.

In his speculations on the constitution of the benzene derivatives, the author discusses at length the relative positions occupied by the substituting radicals in various benzene and phenol derivatives, but it

would be impossible, without entire reproduction of the memoir, to explain the argument involved in each case. The general conclusions at which he arrives will be understood on inspection of the following classified list of various isomeric di-derivatives of benzene:—

Meta-series, 1 : 2.	Ortho-series, 1 : 3.	Para-series, 1 : 4.
Phthalic acid, m.-p. 185°.	Isophthalic acid, m.-p. over 300°.	Terephthalic acid, sublimes above 300° without melting.
Salicylic acid, m.-p. 157°.	Oxybenzoic acid, m.-p. 199°.	Paroxybenzoic acid, m.-p. 210°.
Metamidobenzoic acid, m.-p. 144°.	Orthamidobenzoic acid, m.-p. 173°.	Paramidobenzoic acid, m.-p. 187°.
Metachlorobenzoic acid, m.-p. 137°.	Orthochlorobenzoic acid, m.-p. 153°.	Parachlorobenzoic acid, m.-p. 237°.
Pyrocatechin, m.-p. 112°.	Resorcin, m.-p. 99°.	Hydroquinone, m.-p. 178°.
Metachlorophenol, liquid.	——	Parachlorophenol, m.-p. 41°.
Metanitrophenol, m.-p. 45°.	——	Paranitrophenol, m.-p. 110°.
——	Dinitrobenzene, m.-p. 87°.	Dibromobenzene, m.-p. 89°.
Metanitrobromobenzene, m.-p. 38°.	Orthonitrobromobenzene, m.-p. 56°.	Paranitrobromobenzene, m.-p. 125°.
Metanitraniline, m.-p. 38°.	Orthonitraniline, m.-p. 108°.	Paranitraniline, m.-p. 146°.
Metabromaniline, m.-p. 31°.	Orthobromaniline, liquid.	Parabromaniline, m.-p. 64°.
Metadiamidobenzene, m.-p. 99°.	Orthodiamidobenzene, m.-p. 64°.	Paradiamidobenzene, m.-p. 140°.

It will be evident that the arrangement is very different from that usually adopted. Many derivatives hitherto supposed to be members of the 1 : 3 series are placed in the 1 : 2 (phthalic) series; derivatives usually assumed to belong to the 1 : 2 series are placed in the 1 : 4 (terephthalic) series; and many of those hitherto regarded as 1 : 4 derivatives are arranged in the 1 : 3 series. Thus dinitrobenzene and resorcin, for example, two bodies which have hitherto always been regarded as 1 : 4 derivatives, are placed by the author in the isophthalic series. This conclusion is arrived at by a somewhat novel and daring train of argument: the resemblance between benzene and toluene on the one hand, and between dinitrobenzene and dinitrotoluene on the other, the author argues is perfect,* therefore the nitro-groups in the two compounds occupy relatively the same position; now it may be shown that dinitrotoluene has the constitution 1 : 2 : 4, and that the nitro-groups occupy the positions 2 and 4. If then the nitro-groups in dinitrobenzene occupy the same relative positions as in dinitrotoluene, it follows that the former is a 1 : 3 derivative. Again, non-volatile nitrophenol, the crystalline modification of chlorophenol, and hydroquinone, which have been regarded as members of the

* He does not tell us in what respects.

phthalic, are placed by the author in the terephthalic series in virtue of the following considerations: Nitranisic acid must be 1 : 2 : 4—anisic acid being a member of the 1 : 4 series, the position 1 being occupied by the group OCH_3,—since on further nitration it yields a dinitranisol, from which, by the action of ammonia, a dinitraniline is obtained, which on removal of the NH_2 group yields ordinary dinitrobenzene (Salkowski)—the CO_2H group in nitranisic acid being replaced by NO_2 when it is acted upon by nitric acid. The same dinitraniline is obtained by the action of ammonia on dinitrobromobenzene, which it has been shown may be directly converted into α-dinitrophenol by heating with alkalies: hence the constitution of α-dinitrophenol must also be 1 : 2 : 4—(OH at 1); and since both the known modifications of mononitrophenol yield α-dinitrophenol on nitration, one of them must be a 1 : 2, the other a 1 : 4 derivative. Now Salkowski has shown that nitranisic acid (1 : 2 : 4) may be converted by the action of ammonia into nitroparamidobenzoic acid, and that on reduction this yields a diamidobenzoic acid (1 : 2 : 4—CO_2H at 4), which is split up on distillation into carbonic anhydride and the modification of phenylenediamine first described by Griess (m.p. 99°); this latter must consequently be a 1 : 2 derivative. Zincke and Sintenis have shown that the same phenylenediamine is obtained by the action of ammonia on the modification of nitrobromobenzene which melts at 38°, which they on the other hand succeeded in converting into the volatile modification of nitrophenol. Volatile nitrophenol is therefore a member of the phthalic series, and the non-volatile modification is thus proved to belong to the terephthalic series, and since it has been directly converted into crystalline chlorophenol, and this by fusion with potassium hydrate into hydroquinone, it follows that these two bodies are also members of the terephthalic series.

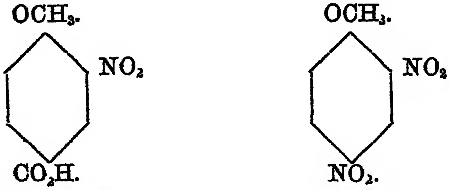
The constitution of the various haloid derivatives of phenol and the nitrophenols is also discussed by the author.

H. E. A.

Note on the Above. By H. Salkowski (Deut. Chem. Ges. Ber., vi, 608—611).

The author has previously stated that nitranisic acid is converted by the action of nitric acid into dinitranisol, and that dinitranisic acid yields the same dinitranisol when similarly treated.

Petersen assumes that, in the conversion of nitranisic acid into dinitranisol, the CO_2H group becomes replaced by NO_2, thus—



Nitranisic acid. Dinitranisol.

But since the formation of the same dinitranisol from dinitranisic acid cannot be reconciled with his assumption that the nitro-groups in dinitrobenzene occupy relatively the positions 1 : 3, he suggests that Salkowski's statement is incorrect, and that the compound he examined was a mixture of an isomeric dinitranisol with trinitranisol. This Salkowski entirely repudiates; in the interval he has re-examined the behaviour of dinitranisic acid with nitric acid, and has again obtained results which lead him to abide by his former statements in their entirety. Moreover, Petersen's assumption is improbable, simply by reason of the fact that dinitranisol cannot be further nitrated by nitric acid alone, even the strongest.

H. E. A.

Action of Heated Lead Oxide on Organic Bodies. By A. BEHR and W. A. VON DORP (Deut. Chem. Ges. Ber., vi, 753—755).

THE action of heat on aromatic hydrocarbons results in most cases in the elimination of hydrogen, and condensation. For example, from benzene in this way are produced diphenyl and diphenyl-benzene. It was to be expected that the presence of an oxidising agent would facilitate the reaction by assisting in the removal of the hydrogen, and with this view the authors have employed lead oxide. The vapour of the organic body was passed over the oxide gently heated in a glass tube.

Acenaphthene treated in this way gave a crystalline hydrocarbon melting at 92°—93°, and to which analysis assigned the formula $C_{12}H_8$. It was therefore acetylene-naphthalene, $C_{10}H_6{<}\begin{matrix}CH\\ \|\\ CH\end{matrix}$.

Dibenzyl furnished very considerable quantities of stilbene, recognisable by the melting-point, crystalline form, and characters of the dibromide. A small quantity of another hydrocarbon, not yet isolated, was produced at the same time.

Benzyl-toluene gave much anthracene.

Experiments were also made with some bodies containing oxygen.

A liquid and a solid modification of tolyl-phenyl ketone have been described by Kollarits and Merz. The liquid variety, in contact with gently heated lead oxide, furnished considerable quantities of anthraquinone, whilst the solid gave no trace of it. In confirmation of this result, the authors found that the liquid ketone passed over heated zinc dust gave anthracene, whilst the solid furnished little anthracene, but another body which seemed to be benzyl-toluene.

Aniline vapour passed over heated oxide of lead yielded a small quantity of a base which crystallises in needles and melts at 170°.

W. A. T.

Chlorotoluenes. By H. HÜBNER and W. MAJERT (Deut. Chem. Ges. Ber., vi, 790—795).

BY treating the hydrochloride of the amidotoluene derived from solid nitrotoluene, with hydrochloric acid, passing in nitrous acid, and dis-

tilling the product, a mixture of chlorotoluene, cresol, nitro-cresol, and nitrotoluene was obtained. When isolated, this chlorotoluene, which corresponds to the solid bromotoluene, was found to boil at 160·5° and melt at 6·5°.

When the monochlortoluenes obtained by chlorinating toluene in presence of iodine, are dissolved in fuming sulphuric acid and converted into barium salts, it is found that three isomeric salts are obtained. Two of these, the ortho- and β-para salts, coincide in crystalline form, &c., with the salts of the corresponding bromo-acids; but the third, which is probably derived from the solid chlorotoluene, appears to differ somewhat in external properties from the bromine-compound.

Salts of Orthochlorotoluene-sulphonic acid, $C_6H_3CH_3{}^iCl^{ii}(SO_2OH)$. *Barium salt*, $(C_6H_3ClCH_3SO_2O)_2Ba + 2H_2O$: small elongated rhombic leaflets which acquire a pearly lustre on drying and begin to lose water at 180°. *Calcium salt* $(C_6H_3ClCH_3SO_2O)_2Ca + H_2O$: stellar groups of long flat crystals, which lose water over sulphuric acid. *Lead salt* $(C_6H_3ClCH_3SO_2O)_2Pb + 2H_2O$: rosettes of short lustrous needles. *Potassium salt*, $C_6H_3ClCH_3SO_2OK + \frac{1}{2}H_2O$: large colourless quadratic tables which have a pearly lustre, are truncated at the corners, and often form step-like masses. They lose water at 140°. The *sodium salt*, $C_6H_3ClCH_3SO_2ONa + \frac{1}{2}H_2O$, resembles the potassium salt, but is more soluble. The *copper salt* forms beautiful blue crystals belonging to the regular system, and having well-defined faces. *Copper-ammonium salt*: fine dark blue crystals, belonging to the regular system. *Ammonium salt*, $C_6H_3ClCH_3SO_2ONH_4$: rosettes of colourless flat crystals.

Salts of Orthochlorosulphobenzoic acid. The *acid potassium salt*, $C_6H_3Cl\begin{cases}SO_2OK\\COOH\end{cases} + H_2O$, was obtained by oxidising orthochlorotoluene-sulphonic acid by means of potassium bichromate and sulphuric acid, and neutralising the product with barium carbonate; it then separates in long fine needles resembling asbestos. *Barium salt*, $C_6H_3Cl\left.\begin{matrix}SO_2O\\COO\end{matrix}\right\}Ba + H_2O$: forms stellate groups of ill-defined needles. *Lead salt*, $C_6H_3Cl\left.\begin{matrix}SO_2O\\COO\end{matrix}\right\}Pb + H_2O$: nodular masses.

Barium metatoluene-sulphonate, obtained by treating the free acid with sodium amalgam, and neutralising the acid obtained from the sodium salt with barium carbonate, forms colourless transparent nodular crystals.

Salts of β-parachlorotoluene sulphonic acid, $C_6H_3Cl^{iv}CH_3{}^i(SO_2OH)$. *Barium salt* $(C_6H_3CH_3ClSO_2O)_2Ba + H_2O$: crystallises either in amber-yellow nodules, clear transparent crusts, or microscopic leaflets. When prepared from the crystallised parachlortoluene, it forms large tables. It dissolves in 33 parts of water at 14·5°.

The *calcium salt*, $(C_6H_3CH_3ClSO_2O)_2Ca + 6H_2O$, was obtained, on one occasion, in small truncated tables, and, at another time, in small elongated leaflets. The crystals lose water on exposure to the air. *Lead salt* $(C_6H_3CH_3ClSO_2O)_2Pb + 8H_2O$: white needles which lose water in the air. *Potassium salt*, $C_6H_3ClCH_3SO_2OK + H_2O$: small colourless needles, which acquire a silky lustre on drying. *Copper salt* $(C_6H_3ClCH_3SO_2O)_2Cu + 7H_2O$: large bright blue leaflets. *Copper-*

ammonium salt; crusts of small compact needles having a deep indigo-blue colour. They effloresce on exposure to the air.

Salts of α-parachlorotoluene-sulphonic acid, $C_6H_3Cl^{iv}CH_3^{i}(SO_2OH)$ (?). *Barium salt* $(C_6H_3ClCH_3SO_2O)_2Ba + \frac{1}{2}H_2O$; lance-shaped crystals, which, when recrystallised, form small shining leaflets. It is not efflorescent, and it dissolves in 7 parts of water at 14·5°. *Sodium salt*, $C_6H_3ClCH_3SO_2ONa + 5H_2O$; crystallises in lance-shaped needles, short needles or long shining quadrats, according to the concentration of the solution.

It is intended to study the sulpho-acids derived from the solid chlortoluene, and also the nitro- and amido-derivatives of the three chlorotoluenes.

The authors consider it probable that when cold toluene is chlorinated in presence of iodine, the chlorine unites with the hydrocarbon, forming a dichloride which afterwards splits up into methylmonochlorobenzene and hydrochloric acid; but when chlorine acts on hot toluene, the dichloride is not formed, the methyl being attacked directly.

T. B.

Terebene. By J. RIBAN (Compt. rend., lxxvi, 1547—1550).

THE liquid resulting from the distillation of turpentine oil from oil of vitriol, and to which the name of terebene has been given, is a mixture of pure terebene and cymene. Pure terebene, $C_{10}H_{16}$, is a colourless, mobile liquid, boiling at 155°—156°, which remains fluid even at − 27°. Its sp. gr. at 0° = 0·877, at 20° = 0·860, at 40° = 0·843. Its vapour-density is 4·79, by calculation 4·70. It is less oxidisable than terebenthene, and it has no action on polarised light. A mixture of alcohol and nitric acid does not convert it into a crystalline hydrate. Dry hydrochloric acid converts it into crystalline terebene monochlorhydrate, $C_{10}H_{16}.HCl$, decomposible by boiling water, with elimination of HCl and formation of a crystalline camphene. No terebene subchloride can be formed by the above reaction. The substance commonly known by that name is a solution of the terebene monochlorhydrate in cymene. When antimonic chloride is added, in small portions at a time, to terebene, and a gentle heat is applied, the terebene becomes viscid. The new compound is washed, first with cold alcohol, and then with hot; it is then dissolved in ether, the latter is distilled off and the residue is kept, *in vacuo*, at 210°. The polymeride, tetra-terebene, $C_{40}H_{64}$, thus formed, is a nearly colourless, transparent solid, having a conchoidal fracture.

The cymene obtained in the preparation of terebene was probably formed by the following reaction:—

$$C_{10}H_{16} + H_2SO_4 = C_{10}H_{14} + SO_2 + 2H_2O.$$

(See, however, this volume, p. 700.) It may also be obtained from pure terebene, although not so easily.

B. J. G.

New Derivatives of Naphthalene. By J. P. BATTERSHALL (Ann. Chem. Pharm., clxviii, 114—126).

THE results contained in the first part of this paper have been published in this Journal ([2], x, 698). The following salts of α-sulphonaphthoic acid were prepared. $C_{10}H_6(SO_3)(CO_2)Ba + 4H_2O$ forms well-defined glistening, transparent, and compact monoclinic crystals. $C_{10}H_6(SO_3)CO_2Ca + 3H_2O$ is tolerably soluble in water, and crystallises in thin plates. $C_{10}H_6(SO_3K)(CO_2K) + 2H_2O$ forms thin tables and is freely soluble in water. $C_{12}H_6(SO_3)(CO_2)Cu$ is a bluish-green precipitate, which is sparingly soluble in boiling water.

α-Oxynaphthoic acid, $C_{10}H_6(OH)CO_2H$, is obtained by gradually adding potassium α-sulphonaphthoate to fused potash. It dissolves freely in alcohol and with moderate facility in boiling water, and crystallises from a hot aqueous solution in long interlaced needles, melting at 234°—237°, and subliming, when carefully heated, in feathery crystals. On boiling down the aqueous solutions of their salts, the liquid darkens and a dark amorphous mass separates out.

Sulpho-isonaphthoic acid, $C_{10}H_6(SO_3H)(CO_2H)$, is produced by dissolving isonaphthoic acid in fuming sulphuric acid. It forms a very characteristic acid barium salt, $(C_{11}H_7SO_5)_2Ba + 7H_2O$, which is almost insoluble in cold water, and crystallises from a boiling solution in brilliant large plates. The neutral salt, $C_{11}H_6SO_5Ba + H_2O$, is readily soluble in water, and forms oblique crystals.

On fusing the potassium salt with potash, it yields *oxyisonaphthoic acid*, $C_{10}H_6(OH)CO_2H$, crystallising from boiling water in long needles, melting at 212°—213°. Its salts are as unstable as the α-oxynaphthoates.

C. S.

Trinitronaphthalene. By F. BEILSTEIN and A. KUHLBERG (Deut. Chem. Ges. Ber., vi, 647—649).

THE authors prepare the trinitronaphthalene by boiling one part of the dinitronaphthalene for a few minutes with 5 of fuming nitric acid and 5 of concentrated sulphuric acid. The *β-trinitronaphthalene* prepared from β-dinitronaphthalene melts at 213°, and is characterised by being but very slightly soluble in alcohol. It is identical with the β-trinitronaphthalene of Laurent. On treating α-dinitronaphthalene, however, with the nitrating mixture, another modification, *γ-trinitronaphthalene* is obtained quite distinct from the α-trinitronaphthalene which Aguiar prepared by prolonged digestion of α-dinitronaphthalene with fuming nitric acid. It crystallises from fuming nitric acid in bright yellow quadrilateral tables which melt at 147°. The tetranitronaphthalenes can be readily obtained from dinitronaphthalene by employing twice as much of the nitrating mixture in which fuming sulphuric acid is substituted for the ordinary acid.

C. E. G.

A Glycerin of the Aromatic Series. By E. GRIMAUX (Compt. rend., lxxvi, 1598—1602).

THE author describes the preparation and properties of phenylglycerin, $C_3H_4(C_6H_5)(OH)_3$, which he has obtained in the following manner:—

Cinnyl alcohol (styrone) dissolved in chloroform was converted into styrone dibromide, $C_9H_9Br_2OH$, by the addition of bromine to the well-cooled solution; this alcohol crystallises in large colourless scales, or groups of fine needles, insoluble in water, but easily soluble in alcohol and ether; it melts at 74°. By the action of acetic chloride styrone dibromide is converted into the acetyl-derivative, $C_9H_9Br_2C_2H_3O_2$, which crystallises in well formed oblique prisms and possesses an agreeable odour of flowers; it melts at 85°—86°. By the action of hydrobromic acid on styrone dibromide, or of bromine on cinnyl bromide, C_9H_9Br, the tribromide, $C_9H_9Br_3$, is obtained; it crystallises from chloroform in small needles, slightly soluble in alcohol and ether, and melts at 124°. By the addition of bromine to cinnyl chloride the chlorodibromide, $C_9H_9ClBr_2$, is obtained; it crystallises from ether in transparent plates, which melt at 96·5°.

On heating styrone dibromide with water either in closed tubes, or open vessels, it is partially converted into phenylglycerin, or *stycerin*, as the author terms the new compound; but at the same time a quantity of matter insoluble in water is formed, which probably consists of condensation-products. To avoid the formation of these, and to remove the hydrobromic acid as it is produced, the author boils the styrone dibromide with water and argentic acetate; after 48 hours' digestion the solution is filtered, freed from silver by sulphuretted hydrogen, concentrated, and dried in a vacuum. Thus obtained, stycerin is a pale yellow gummy mass, excessively soluble in water and alcohol, scarcely soluble in ether; it has a distinct bitter taste.

H. E. A.

Action of Nascent Hydrogen on Bitter-Almond Oil. By H. AMMANN (Ann. Chem. Pharm., clxviii, 67—81).

WHEN a cold solution of bitter-almond oil in aqueous alcohol is treated with sodium amalgam, hydrobenzoin is formed, together with a compound having the same composition but melting at 119°, and a considerable proportion of benzyl alcohol. If, on the other hand, the bitter almond oil is digested with water and sodium amalgam, a considerable proportion of the substance melting at 119° is formed, and but a small amount of hydrobenzoïn or benzyl alcohol. By repeatedly crystallising the first product from alcohol, the hydrobenzoin was obtained in a pure state; and by crystallising the second product from alcohol, the compound melting at 119° was obtained pure. The author calls this substance *isohydrobenzoïn*.

Action of Acetyl Chloride on Hydrobenzoïn.—Hydrobenzoïn was dissolved in acetyl chloride, and the solution was allowed to remain for twenty-four hours, after which the solvent was removed by means of a current of air. The residue consisted of a mass of shining needles

which, when crystallised from alcohol, melted at 133°—134°, and had the composition $C_{14}H_{12}\langle{}^{OC_2H_3O}_{OC_2H_3O}$.

Action of Phosphoric Chloride on Hydrobenzoïn.—When one molecule of hydrobenzoïn and two molecules of phosphoric chloride are placed in a retort and either allowed to remain in contact, or gently heated, an energetic reaction takes place, and on cooling, colourless crystals separate. The new substance, which the authors propose to call *hydrobenzoïn chloride*, was purified by washing with water and crystallisation from toluene. It forms large colourless needles melting at 188°, and possessing the composition $C_{14}H_{12}Cl_2$.

Isohydrobenzoïn, $C_{14}H_{14}O_2$, separates from water in thin shining quadratic prisms, which contain water and effloresce on exposure to the air. In alcohol, it is rather more soluble, and in water rather less soluble, than hydrobenzoïn, one part requiring for solution 80 parts of hot water or 526 of water at 15°. It separates from alcohol in compact anhydrous crystals which belong to the hexagonal system, and melts at 119·5°. Sodium amalgam has no action on it, and it yields with nitric acid an oily product, whereas hydrobenzoïn yields benzoïn with this reagent.

Action of Acetyl Chloride on Isohydrobenzoïn.—When isohydrobenzoïn is treated with acetyl chloride, as described in the case of hydrobenzoïn, a thick oil is obtained which, after several crystallisations from alcohol, took the form of shining leafy crystals, melting at 117° —118°. This substance was found to have the same composition as the aceto-derivative of hydrobenzoïn.

Action of Phosphoric Chloride on Isohydrobenzoïn.—The action between these substances resembles that between phosphoric chloride and hydrobenzoïn, but it is more energetic, and the products appear to be identical in each case.

The author remarks that a comparison of isohydrobenzoïn with the toluylene alcohol and isotoluylene alcohol of Limpricht and Schwanert would be useless, as these are evidently mixtures. When the former is treated with acetyl chloride, it yields an acetate melting at 116°; consequently it contains isohydrobenzoïn, and with nitric acid it yields benzoïn, hence it evidently contains hydrobenzoïn.

The following portion of the paper is by Fittig, he having continued the investigation in consequence of the death of the author.

Action of Alcoholic Potash on Hydrobenzoïn Chloride.—When these substances are digested together until most of the alcohol is removed, and the product, after solution in water, is acidified with hydrochloric acid, a layer of chemically pure tolane is found floating on the liquid. This reaction affords a convenient method of obtaining small quantities of pure tolane. The chloride obtained from isohydrobenzoïn reacts similarly with alcoholic potash, but the product does not appear to be so pure as in the former case.

Fittig did not succeed in obtaining the substance which Limpricht and Schwanert describe as being formed by the action of dilute sulphuric acid on hydrobenzoïn, but he obtained an oil which, when distilled with water, yielded a resinous amorphous residue.

T. B.

Dichlorobenzoic Acid. By A. CLAUS (Deut. Chem. Ges. Ber., vi, 721—723).

BY the action of potassium chlorate and dilute hydrochloric acid on benzoic acid in diffused daylight, not only monochlorobenzoic acid is formed, as Otto has stated, but also a dichlorobenzoic acid, crystallising from hot water in soft, silky, interlaced needles melting at 156°, and subliming without decomposition. $(C_7H_3Cl_2O_2)_2Ba + 3H_2O$ forms thin, long, lustrous needles, dissolving in 12·5 parts of water at 28°. $(C_7H_3Cl_2O_2)_2Ca + 2H_2O$ crystallises in fine, radiated needles.

Beilstein's dichlorobenzoic acid, which he obtained by oxidising dichlorotoluene and by the action of bleaching powder on benzoic acid, melts at 201°; its calcium salt contains 3 molecules of water, and the barium salt 4 molecules; the latter is very sparingly soluble, 1·1 part dissolving in 100 parts of water at 18°. Otto converted dichlorohippuric acid into a dichlorobenzoic acid melting at 196°—197°; its calcium and barium salts have, however, the same composition and crystalline shape as those obtained by the author.

C. S.

Preliminary Notice on the Action of Sodium Amalgam on Dinitrobenzoic Acid. By VICTOR MEYER and W. MICHLER (Deut. Chem. Ges. Ber., vi, 746—748).

DINITROBENZOIC acid dissolved in solution of soda and treated with sodium amalgam, gives a black liquid which, on being neutralised by hydrochloric acid, deposits a black flocculent precipitate. When dry, this precipitate appears as a black velvety powder insoluble in water, alcohol, ether, benzene, and acetic acid. The salts are black and amorphous like the acid itself. Analysis of the zinc, silver and barium salts lead to the formula, $C_6H_3\left\{\begin{matrix}CO.OH\\ N\\ N\end{matrix}\right.O$, which represents it as diazoxybenzoic acid.

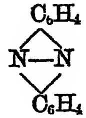
This body bears so strong a resemblance to the substances known as humus, which by some chemists are considered to be nitrogenous, that the authors are led to the conjecture that it may really be a representative of this obscure class of compounds.

W. A. T.

Azophenylene. By A. CLAUS (Ann. Chem. Pharm., clxviii, 1—21; also Deut. Chem. Ges. Ber., vi, 723—726).

AN abstract of this investigation has already been published in this Journal (1872, p. 694). The present paper gives a full description of the preparation and purification of the different compounds, and contains the following new facts:—

All the reactions of azophenylene are best explained by assuming the following structural formula:—



But then arises the question how this body is derived from azobenzoic acid, $C_{14}H_{10}N_2O_4$, which, according to Strecker, stands in the same relation to azobenzene as benzoic acid to benzene, and therefore ought to yield azobenzene by the dry distillation of its calcium salt. Most probably azobenzoic acid contains two atoms of hydrogen less; this view is supported by the following facts. If this acid corresponded to azobenzene, its formation would be explained by the following equation:—

$$2C_7H_5NO_4 + 8Na + 4H_2O = 8NaOH + C_{14}H_{10}N_2O_4.$$

But by using this quantity of sodium in the form of amalgam it was found that as soon as three-fourths was added a brisk evolution of hydrogen commenced, showing that the reaction was finished,—

$$2C_7H_5NO_4 + 6Na + 2H_2O = 6NaOH + C_{14}H_8N_2O_4.$$

Azobenzoic acid is therefore *azophenylene-dicarbonic acid*, and most probably identical with *azodracylic acid*, which, by distilling its calcium salt, also yields azophenylene, in which compound therefore the two nitrogen atoms occupy the position 3 : 4. Metazobenzoic acid also yields azophenylene. C. S.

Brominated Benzene-sulphonic Acids. By A. WOELZ (Ann. Chem. Pharm., clxviii, 81—93).

Dibrombenzene-sulphonic Acid.—Dibromobenzene was dissolved in sulphuric acid heated to 80°—90°, and the solution, after dilution, was neutralised with barium carbonate. The barium was removed from the solution by means of sulphuric acid, and the liquor, when evaporated, yielded the acid in tabular crystals. This acid is extremely soluble in water, alcohol, or ether, and its crystals, which have the composition $C_6H_3Br_2SO_3H + 3H_2O$, are slightly efflorescent, and lose 2 molecules of water at 100°, the residue melting at about 132°. The *barium salt*, $(C_6H_3Br_2SO_3)_2Ba$, forms slender pearly rhombic leaflets, which are slightly soluble in cold water or alcohol, but easily soluble in hot water. *Calcium salt*, $(C_6H_3Br_2SO_3)_2Ca + 9H_2O$: tufts of silky needles, which effloresce on exposure to the air. It is easily soluble in water, and tolerably soluble in alcohol. *Potassium salt*, $C_6H_3Br_2SO_3K + H_2O$: tufts of shining needles, which are easily soluble in water or alcohol. *Ammonium salt*, $C_6H_3Br_2SO_3,NH_4$: slender shining needles or compact tabular crystals, very soluble in water. *Copper salt*, $(C_6H_3Br_2SO_3)_2Cu + 14H_2O$: easily soluble, elongated leafy blue crystals, which effloresce on exposure to the air. *Lead salt*, $(C_6H_3Br_2SO_3)_2Pb + 3H_2O$: shining rhombic leaflets, which dissolve pretty easily in water.

The potassium salt of this acid was fused with potash and the product was neutralised and treated with ether in the usual way. The ethereal solution yielded only a small quantity of a pasty brown product, which gave a violet colour with iron chloride. When this

substance was distilled, a few oily drops were obtained, which solidified on cooling.

When the potassium salt of dibromobenzene-sulphonic acid was mixed with potassium cyanide and subjected to dry distillation in a stream of carbonic anhydride, ammonium sulphide and sulphite passed over, together with some drops of an oily substance which, when crystallised from alcohol, yielded needle-shaped crystals insoluble in water and melting at about 112°. It is probable that this substance consists of *tricyanobenzene*. When the above-mentioned oily product was digested with alcoholic potash, ammonia was evolved, and the residue, when neutralised and agitated with ether, yielded a small quantity of an acid crystallising in needles. This acid is easily soluble in hot water, alcohol, or ether, but it is almost insoluble in cold water. It melts with partial decomposition at 149°—150°, and the salts which it forms with calcium and barium are soluble in water, but have not much tendency to crystallise. The amount of barium in the latter indicated the formula $C_6H_3(COO)_3HBa$.

Monobromobenzene-sulphonic Acids.—The potassium salt of the acid which Garrick obtained by the bromination of benzene-sulphonic acid was fused with potash and found to yield resorcin. Thinking that, perhaps, hydroquinone might be first formed, and afterwards transformed into resorcin, the author fused some pure hydroquinone with potash, but no trace of resorcin was formed, the hydroquinone being unaltered.

When the potassium salt of the above-mentioned acid was distilled with potassium cyanide a small quantity of an oily distillate was obtained. This oil was found to be a mixture of benzonitrile and a solid nitrile, which melted at 150°—160° and yielded terephthalic acid on treatment with alcoholic potash.

The acid which Garrick obtained by the action of sulphuric acid on monobrombenzene also yielded resorcin when fused with potash, and the author remarks that the non-identity of Garrick's two monobrombenzene-sulphonic acids cannot be considered as at present definitively established. T. B.

Synthesis of Piperonylic Acid, and a New Method of Forming the Aldehyde of Protocatechuic Acid. By FITTIG and REMSEN (Ann. Chem. Pharm., clxviii, 93—95).

IN order to confirm their view that piperonylic acid is methylene-protocatechuic acid, the authors heated together 1 molecule of protocatechuic acid, 3 molecules of potassium hydrate, and $1\frac{1}{2}$ molecule of methylene iodide, first at 100° and afterwards at 110°. The product was boiled with potash in order to decompose any ether of methylene-protocatechuic acid that might be present; water was then added and the whole was acidified with hydrochloric acid. Under these circumstances a brown amorphous precipitate was formed; and the filtrate from this yielded, on evaporation, brownish crystals, which, after treatment with animal charcoal and sublimation, were found to be identical with piperonylic acid. When an aqueous solution of piperonylic acid from either source is slowly cooled, the acid is deposited in long, white threads resembling sewing cotton.

The decomposition of piperonylic acid into carbon and protocatechuic acid may be effected not only by dilute hydrochloric acid, but also by water. In the latter case, however, the temperature required is so high that the protocatechuic acid splits up into pyrocatechin and carbonic anhydride.

When piperonal is heated with dilute hydrochloric acid it is decomposed in an analogous manner, the aldehyde of protocatechuic acid being formed—

$$C_6H_3\begin{cases}-O\\-O\\-CHO\end{cases}\!\!>C\begin{cases}H\\H\end{cases} = C_6H_3\begin{cases}OH\\OH\\CHO\end{cases} + C.$$

The liquor filtered from the deposited carbon yielded, on evaporation, crystals of the aldehyde, which was found to be identical with that already described by the authors.

T. B.

Ethene-protocatechuic Acid. By R. FITTIG and T. MACALPINE (Ann. Chem. Pharm., clxviii, 99—114).

THIS acid is readily produced by heating protocatechuic acid with potash, a little water, and an excess of ethene dibromide in sealed tubes to 100°. It crystallises from boiling water in brilliant broad needles, and from alcohol in short glistening prisms, melting at 133·5°, and subliming when carefully heated. It is more freely soluble in hot water than piperonylic acid (methene-protocatechuic acid). The calcium salt, $(C_9H_7O_4)_2Ca + 2H_2O$), is sparingly soluble in cold water, and crystallises in large monoclinic prisms, the measurements of which are given. $(C_9H_7O_4)_2Ba + 2H_2O$ forms brilliant, transparent, compact, oblique crystals. The sodium salt is very soluble, and does not crystallise well. The solutions of these salts give with ferric chloride a yellow precipitate like the piperonylates. The ethyl-ether, $C_9H_7O_4.C_2H_5$, crystallises, when an alcoholic solution is allowed to evaporate at a low temperature in hard prisms, which, after being dried in an exsiccator, melt at 27°—28°.

When ethene-protocatechuic acid is heated with dilute hydrochloric acid to 260° it is decomposed, much carbonaceous matter and gases containing no acetylene being formed, and a trace of pyrocatechin. On heating ethene-protocatechuic acid gently with phosphorus pentachloride, it is converted into the corresponding chloride; at the same time some chloride of dichlorethene-protocatechuic acid is produced, which is obtained in larger quantity by heating the substances in closed tubes. Water decomposes it into hydrochloric acid and *dichlorethene-protocatechuic acid*, $C_9H_6Cl_2O_4$, which is insoluble in cold water, and is obtained as a white precipitate, by dissolving the product in a dilute solution of sodium carbonate, and adding hydrochloric acid to the filtered liquid. On boiling it with water, it yields protocatechuic acid, hydrochloric acid, and probably glycollic acid. These reactions may be explained by the following equations:—

$$(1)\ C_6H_3\begin{cases} O \\ O \end{cases}\!\!>C_2H_4 \\ \ \ CO_2H \quad + PCl_5 = C_6H_3\begin{cases} O \\ O \end{cases}\!\!>C_2H_4 \\ \ \ COCl \quad + POCl_3 + HCl.$$

$$(2)\ C_6H_3\left\{\begin{array}{l} O\!\!>C_2H_4 \\ O \\ COCl \end{array}\right. + 2PCl_5 = C_6H_3\left\{\begin{array}{l} O\!\!>C_2H_2Cl_2 \\ O \\ COCl \end{array}\right. + 2PCl_3 + 2HCl.$$

$$(3)\ C_6H_3\left\{\begin{array}{l} O\!\!>C_2H_2Cl_2 \\ O \\ COCl \end{array}\right. + H_2O = C_6H_3\left\{\begin{array}{l} O\!\!>C_2H_2Cl_2 \\ O \\ CO.OH \end{array}\right. + HCl.$$

$$(4)\ C_6H_3\left\{\begin{array}{l} O\!\!>C_2H_2Cl_2 \\ O \\ CO.OH \end{array}\right. + 3H_2O = C_6H_3\left\{\begin{array}{l} OH \\ OH \\ CO.OH \end{array}\right. + 2HCl + C_2H_4O_2.$$

Carbohydroquinonic acid, which is produced by the action of bromine on an aqueous solution of quinic acid, is, according to Hesse, isomeric with protocatechuic acid, while other chemists believe the two acids to be identical. To settle this question, carbohydroquinonic acid was treated with potash and ethene dibromide, and thus an acid obtained having all the characteristic properties of ethene-protocatechuic acid. Ethyl protocatechuate forms glistening prisms, melting at 133°—134°, and agreeing in all other respects with Hesse's ether.

C. S.

A Curious Reaction of Benzoic, Salicylic, and Hippuric Acids.

By T. L. PHIPSON (Chem. News, xxviii, 13).

THREE equivalents of benzoic or salicylic acid and one of glucose warmed with a large excess of strong sulphuric acid, develop a fine blood-red colour. Benzoic acid alone does not produce this colour. Hippuric acid gives the same reaction, but the mixture speedily blackens and evolves a large quantity of carbon monoxide.

M. J. S.

Aromatic Amido-Acids containing Alcohol-radicals.

By PETER GRIESS (Deut. Chem. Ges. Ber., vi, 585—588).

THE author finds that three atoms of the hydrogen contained in certain aromatic amido-acids, may be replaced by alcohol-radicals, and that the compounds so formed do not retain the acid characteristics of the original substances, although those derivatives in which only two atoms of hydrogen are replaced, retain, to some extent, the acid properties of the amido-acids.

The amido-acids having three atoms of hydrogen replaced by alcohol-radicals, behave like the base which Hofmann obtained by the action of monochloracetic ether on triethylamine, and appear to be nearly related to the betaine of Scheibler.

Trimethylbenzbetaine, $C_7H_4(CH_3)_3NO_2$, is obtained by allowing a mixture of amido-benzoic acid, methyl alcohol and potash, to remain for some time in contact with methyl iodide, and distilling the mixture. On treating the residue with hydriodic acid, hydriodide of trimethylbenzbetaine was obtained, and by treating an aqueous solution of this with lead hydrate, the free base was produced.

Trimethylbenzbetaine crystallises in small white needles, containing one molecule of water, which is driven off at 105°. It is insoluble in ether, very soluble in alcohol, and does not affect vegetable colours, but possesses a strong bitter taste.

Trimethylbenzbetaine hydriodide is insoluble in ether, but crystallises from water or alcohol in small short prisms. It crystallises with $1H_2O$. *The platinum salt* $[C_7H_4(CH_3)_3NO_2HCl]_2PtCl_4 + 4H_2O$, forms yellow prisms slightly soluble in water.

When the anhydrous base is heated to its melting point, it becomes changed into the isomeric *methylether of dimethylamido-benzoic acid.* This forms an aromatic yellowish liquid, insoluble in water, and boiling at 270° (uncor.). It forms crystalline salts with acids. The *sulphate*, $C_6H_4\left\{\begin{matrix}CO_2CH_3\\N(CH_3)_2\end{matrix}\right\}SH_2O_4$, forms small prisms easily soluble in water, but slightly soluble in dilute sulphuric acid. The *platinum salt*, $(C_6H_4\left\{\begin{matrix}CO_2CH_3\\N(CH_3)_2\end{matrix}\right\}HCl)_2 + PtCl_4$, forms elongated leaflets very slightly soluble in cold water.

When the above ether is heated with strong mineral acids or with alcoholic potash, water is assimilated and methylic alcohol and *dimethylamidobenzoic acid* are formed. This acid forms white needles slightly soluble in water, and melting at 15°.

Trimethylanisbetaine, $C_8H_6N(CH_3)_3O_3$, is prepared like trimethylbenzbetaine, amidoanisic acid being substituted for amidobenzoic acid. It is very soluble in hot water, slightly soluble in alcohol, insoluble in ether, and crystallises from its aqueous solution in large shining prisms containing $5H_2O$. It is neutral to vegetable colours, and has a strong bitter taste. The *hydriodide*, $C_8H_6N(CH_3)_3O_3HI + H_2O$, forms large white shining needles tolerably soluble in hot water or alcohol, insoluble in ether. The *platinum salt*, $[C_8H_6N(CH_3)_3O_3HCl]_2.PtCl_4$, forms small leaflets, very slightly soluble in cold water.

When trimethylanisbetaine is subjected to dry distillation, it is converted into the *methyl ether of dimethylamidanisic acid.* This substance forms a yellowish aromatic liquid, insoluble in water and boiling at 288°.

T. B.

Amidobenzene; and the Preparation of Metadiamidobenzene.

By HUBNER and RETSCHY (Deut. Chem. Ges. Ber., vi, 795—798).

Bromonitro-acetanilide, $C_6H_3BrNO_2NH_3COCH_3$, was prepared by first brominating and then nitrating acetanilide. It forms sulphur-yellow needles melting at 104°. When heated with potash-solution, it yields orange-red needles of *bromonitraniline*, $C_6H_3BrNO_2NH_2$, melting at 110°. Nascent hydrogen converts this latter substance into *diamido*

bromobenzene, which crystallises in fine colourless needles, and melts at 63°. The *sulphate* forms colourless shining leaflets, and the hydrochloride forms colourless needles. The prolonged action of nascent hydrogen on diamidobromobenzene gives rise to a diamidobenzene which was found to be identical with the metadiamidobenzene of Griess.

When bromaniline prepared from the sulphate crystallising in slender leaflets, or from the nitrate, which forms broad or fine needles, was nitrated, it yielded a bromonitramidobenzene, crystallising in orange-red needles and melting at 110°; and this, when acted on by nascent hydrogen, yielded a diamidobromobenzene which crystallised in colourless fine needles, melting at 63°. Its sulphate forms colourless shining leaflets, and its hydrochloride colourless needles. The long-continued action of nascent hydrogen converts it into diamidobenzene, identical with the meta compound of Griess.

During the conversion of bromonitracetanilide into diamidobenzene, a small quantity of a very soluble base having the composition $C_6H_4NNHCH_3C$ is formed. It appears to correspond with the base $C_6H_3CH_3.NNHCH_3C$, which was obtained by Hofman and Hobrecker.

When benzaniline is nitrated and reduced, *monobenzoyldiamidaniline* is obtained. There are, however, indications that a more powerful reduction produces a base analogous to that obtained by the reduction of bromonitracetanilide. T. B.

Action of Chlorine on a Mixture of Phenol and Aniline.

By E. JACQUEMIN (Bull. Soc. Chim. [2], xx, 68—70).

WHEN chlorine-water is added to a mixture of phenol and aniline, a rose-red coloration is produced, which is changed to a deep blue on addition of an alkali. Phenol by itself gives no reaction with chlorine, and aniline, though giving a red coloration with chlorine, does not furnish a blue when an alkali is afterwards added. The blue colour, which is very distinct when a drop of aniline and a drop of phenol are treated with chlorine in four litres of water, is best produced by employing sodium hypochlorite. The author supposes that the blue colour is due to the formation of a new acid, for which he proposes the name *erythrophenic acid*, but he does not adduce any evidence in support of this assumption. B. J. G.

Action of Benzyl Chloride upon Naphthylamine.

By C. FROTÉ and D. TOMMASI (Compt. rend., lxxvii, 57).

BY the action of benzyl chloride upon naphthylamine in presence of a small quantity of zinc powder, a compound $N\begin{cases} C_{10}H_7 \\ H \\ C_7H_7 \end{cases}$ isomeric with cresyl-naphthylamine is obtained. It forms a deep brown uncrystallisable substance, which may be obtained in scales like those of ferric potassio-tartrate. By the action of fuming nitric acid it yields a yellow nitro-derivative. W. A. T.

Preliminary Notice of a New Salt of Quinine.
By P. T. AUSTEN (Pharm. J. Trans. [3], iii, 1016).

WHEN an alcoholic solution of meconic acid is added to an alcoholic solution of quinine, a white curdy precipitate is formed. This precipitate is soluble in hot water, and on cooling, crystals of quinine meconate are deposited. When dried on bibulous paper, the salt has a peculiar sheen, resembling minute fish-scales, and its composition is probably $C_7H_2(C_{20}H_{24}N_2O)''O_7$, corresponding with the silver salt $C_7H_2Ag_2O_7$.

J. B.

Aromatic Phosphorus Compounds. By A. MICHAELIS (Deut. Chem. Ges. Ber., vi, 601—603).

Phosphenyl chloride, $PCl_2(C_6H_5)$, was obtained by repeatedly passing a mixture of phosphorous chloride and benzene through a tube filled with fragments of pumice and heated to low redness. The product when fractionated yielded the new substance as a fuming, highly refractive liquid, boiling at 222°. It has an odour recalling that of hydrochloric acid and that of phosphoretted hydrogen, and is decomposed by water with formation of the corresponding hydroxyl-derivative, together with a small proportion of an oil having a very unpleasant odour. Chlorine converts phosphenyl chloride into a solid, yellowish substance; bromine forms with it a yellowish red solid, and on exposure to the air it becomes converted into a white crystalline mass. Probably these substances correspond with phosphorus pentachloride and oxychloride, but they have not yet been analysed. When phosphenyl chloride is treated with nitric acid, no phosphoric acid is formed, but an acid which appears to be the benzene analogue of the acid, $CH_3PO(OH)_2$.

The author intends to attempt the replacement of the chlorine in phosphenyl chloride by hydrogen and by oxygen, and also to extend his researches to the action of phosphorus trichloride on the homologues of benzene and on the paraffins.

T. B.

The Constituents of Cubebs, with some Remarks on Cubebic Acid. By C. F. SCHULZE (Arch. Pharm. [3], ii, 388—394).

THE original researches on the cubeb berries had for their object the determination of the amount of the essential oil and the extraction of the cubebin. Further investigations led to the formulæ of some of these compounds. Cubeb oil was found to be $C_{15}H_{24}$; cubeb camphor, $C_{15}H_{26}O$; and cubebin, $C_{30}H_{30}O_9$. Bernatzick discovered cubebic acid, and in the *Arch. Pharm.*, cxli, sec. ii, E. A. Schmidt published a prize essay on this subject. The author was at that time engaged in a similar investigation and met with different results.

After some preliminary trials the following process was found to be most applicable:—750 grams of cubebs were treated with 6 litres of

alcohol, the liquid was filtered, and the alcoholic extract distilled. The residue was warmed with sodium hydrate and set aside for some time. It then saponified and crystals were formed under the cake of soap. The latter was repeatedly treated in this manner till it ceased to give further crystals. The crystals were purified by recrystallisation; they left on ignition an alkaline residue, had a bitter taste, and turned brown when exposed to moist air.

Cubebic acid, separated from the sodium salt and purified by means of the lead salt, could not be obtained in the crystalline form. It gave amorphous precipitates with the alkaline earths, and with the heavy metallic oxides; melted at 45°; could not be sublimed; and gave with sulphuric acid a crimson colour, which disappeared on dilution, and changed to brown on addition of nitric acid.

The formula was found to be $C_{14}H_{16}O_4$ (according to Schmidt, $C_{13}H_{14}O_7$).

The residue of the soap, after separation of the oil and cubebin, was treated with hydrochloric acid, and gave a brown resin which could not be purified. The soap in aqueous solution, on treatment with alcohol, gave a fatty oil and cubebin, which latter was recrystallised from hot alcohol and found to agree in its properties with the cubebin discovered by Capitaine and Soubeiran.

W. R.

Essence of Unona odoratissima. By H. GAL (Compt. rend., lxxvi, 1482—1484).

THIS essence is distilled from the flowers of a tree growing in Jamaica; its commercial name is "Alan-gilan." Its specific gravity is ·980; a column of 5 cm. deviates a ray of polarised light 14° to the left; it distils between 160° and 300°; it is soluble in ether, partially soluble in alcohol, insoluble in water. The essence is acted on by potash, which removes benzoic acid. The part insoluble in potash boils between 170° and 300°; from its reactions the author believes it to be a mixture of alcohols, and the original essence to be probably a mixture of benzoic ethers.

R. W.

"Glairin" from the Springs at Molitg. By A. BÉCHAMP (Compt. rend., lxxvi, 1484—1487).

THE amorphous gelatinous deposit of certain sulphurous springs in the Pyrenees appears to consist of gelatinous silica, holding some nitrogenous organic matter; it yields sugar when treated with sulphuric acid. A microscopic examination revealed the presence of an agglomeration of microzymes. Placed in solutions of starch and sugar containing a small quantity of creasote, the glairin developed *bacteria* and other low organisms, while alcohol was formed. Similar solutions without the glairin developed neither organisms nor alcohol.

R. W.

Physiological Chemistry.

Observations on some Liquids of the Organisms of Fish, Crustaceans, and Cephalopods. By L. RABUTEAU and F. PAPILLON (Compt. rend., lxxvii, 135—138).

THIS paper treats of these liquids under the following heads:—

Peritoneal Fluid of various Fish.—There is an abundant liquid in the peritoneal cavity of the rays, having an average sp. gr. 1021, and being neutral, or often slightly acid. It contains a small quantity of a special albuminoïd material, which forms rather a thick layer on the surface when the liquid is evaporated. This fluid when kept gives off an ammoniacal odour resembling that of methylamine. When it is acted on by nitric acid crystals are produced containing a large proportion of urea, but the odour of methylamine which these crystals give off, when treated with potash, proves the presence of another body. It is by the presence of this body that the authors obtain a crystalline hydrochloride on evaporating the liquid and acting on the residue with hydrochloric acid.

The peritoneal fluid of the torpedo and squalus presents nearly identical characters.

Other Liquids.—The analysis of a certain number of both liquid and solid parts of the Plagiostomes shows that they contain a mixture of urea and a *compound urea.*

Digestive Fluids.—The gastric juice of the ray is very acid, and the presence of hydrochloric acid in it was demonstrated. The authors, however, did not find hydrobromic acid, as they might have expected, but all the bromine they found was in the form of a metallic bromide.

Blood.—The blood of the sea-polyps gives no absorption band under the spectroscope. It slowly becomes blue in contact with the air, but loses this blue tint when traversed by a current of carbonic acid gas. Crabs' blood presents the same characters. The blood of the polyps and crabs offers other analogies: they both contain a coagulable substance which cold nitric acid turns yellow, and dissolves when heated, producing a liquid of the same colour. Hydrochloric acid dissolves this substance, forming a pale violet-blue liquid. In the blood of the squalus and ray the authors have found urea in considerable quantities. 85 grams of the blood evaporated and treated with alcohol and acetate of lead yielded no less than 202 c.c. of nitrogen. The authors, in conclusion, admit that their researches are as yet incomplete, owing to the want of appliances at their disposal.

E. C. B.

On Spontaneous Changes occurring in Eggs. By U. GAYON (Compt. rend., lxxvii, 214—217).

THE author in a previous communication announced that the putrefaction of eggs corresponded with the development and multiplication of vibrios in them. He furthermore propounded the theory that these organisms might easily be introduced into the egg during its passage

down the oviduct, and whilst it was being enclosed in the albumin, membranes, and shell. The present communication is intended to complete the author's first results, and to confirm this hypothesis.

It has been announced by previous observers that when eggs are shaken so as to mix the yellow and white, immediate putrefaction occurs. This the author says he has already stated to be far from general. He made an intimate mixture of the yolk and white of egg, passed it into vessels deprived of germs, and kept it for months exposed to pure air at a temperature varying from 20° to 30°. If the experiment be tried with an egg containing bacteria or spores of fungi, and these pass over into the mixture, putrefaction, in the case of the former, and change due to the growth of fungi, in the case of the latter, will occur. In these experiments, as in those of Pasteur, all conditions favourable to spontaneous generation are present, but still it does not occur. The author draws attention to the fact that the molecular granules which are present, especially in the yolk, do not give rise to bacteria. Hence he concludes, in opposition to Béchamp, that the granules which the latter calls *microzymes*, are powerless to convert themselves into bacteria or vibrios, any more than into globules of alcoholic yeast.

The following experiment points to the same results. If during the incubation of an egg the development of the embryo be arrested at any period before the exit of the chick, and if such eggs containing dead embryos be kept for several months at about 25°, some only of them will be found putrified. The others will have undergone a slow non-putrefactive process, similar to that observed in cases of a dead fœtus retained in the abdomen of the mother. Contrary to the hitherto published observations, the author finds that the putrefaction of the embryos of eggs is always accompanied by the development of bacteria or vibrios analogous to those found in the putrefaction of ordinary eggs. The author confirms the views of previous observers that fungi may develop in the interior of eggs and produce special changes. Bacteria and fungi may co-exist, the egg being both putrid and mouldy, but in this case the putrefaction is due to bacteria and not to fungi.

Another change, acid fermentation, has been met with by the author in a few cases. In these the eggs exhale an acid non-putrid odour, and contain, not bacteria, but spicules varying in breadth from ·5 to ·7, and in length from 5 to 10-thousandths of a millimeter.

Lastly, eggs, like all organic matter, may undergo slow oxidation, which does not correspond with the development of any microscopic organisms. This is characterized by a yellow tint of the mixture and the presence of numerous very fine crystalline needles.

In order to support his theory that the organisms above mentioned become enveloped in the egg during its formation, the author examined the oviduct of a recently killed fowl, and found both bacteria and spores of fungi. The number of these microscopic organisms diminishes on passing up the oviduct, but the author has seen them as high as 10 to 15 centimetres from its aperture, and there is no reason why they should not pass still higher, as easily as the spermatozoa with which they are of a size.

E. C. B.

On the Influence of Tea and Coffee on the Amount of Urea excreted.* By E. Roux (Compt. rend., lxxvii, 365).

The interest attaching to this paper lies in the fact that the results arrived at by the author are directly opposed to the generally received idea that tea and coffee diminish the excretion of urea, either by hindering the destruction of tissue, or by giving rise to a more complete assimilation of the substances ingested.

The author premises that as urea is formed partly from the combustion of tissues and partly by the transformation of food, with equal diet and work the amount daily excreted ought to remain nearly constant.

During a period of five months, from the 22nd of March to the 22nd of July, the author kept himself to a regular regimen as regards exercise, diet, and work. In March and April the average daily amount of urea excreted was 33 grams; this rose with the fine weather to 36 grams, and in July again gradually fell to the previous figure.

The amount of water drunk could not have influenced the urea, as, though the quantity of urine varied from 944 to 2515 c.c., the amount of urea remained nearly constant.

The following table shows the results of some of the experiments:—

	Daily quantity of Urea.	Daily quantity of Chlorine.
May 14th to May 18th, without coffee ..	36·18 grams.	4·04 grams.
May 18th, with coffee	41·05 ,,	6·02 ,,
June 16th to June 18th, without tea....	33·76 ,,	5·15 ,,
June 18th, with tea..................	37·04 ,,	7·00 ,,

The increase of urea on the day that coffee was taken is very marked. When, however, the coffee is continued, the urea gradually diminishes till it reaches the normal amount. Tea and coffee likewise produce an increase in the quantity of chlorine excreted. In none of his experiments has the author seen the amount of urea below the normal.

He therefore concludes that, in his person at least, tea and coffee do not retard the destruction of tissues.

Why the effect of these substances seems to diminish with their continued use, whether their first action is to accelerate the elimination of the urea already formed in the tissues, and whether when once this internal washing is over, the normal amount of urea is excreted in spite of the tea and coffee, are questions which the author proposes to himself for future investigations.

E. C. B.

* Or literally, "Variations in the Quantity of Urea Excreted on a Normal Diet, and under the Influence of Tea and Coffee."

Effect of Artificial Addition of Phosphates to the Food of Lambs. By V. HOFMEISTER (*Landw. Versuchs-Stationen*, xvi, 126—183).

Two lots, each consisting of three eight-weeks old wether lambs, were fed from May to December on hay and potatoes, with a little salt, this diet being selected as characteristically poor in phosphates. One lot received precipitated tricalcic phosphate with its food; the other lot none. During the last 77 days most phosphate was given, the phosphatic diet then containing one fourth more phosphate than was supplied by the vegetable food. The lambs gained about 18 lbs. per head in the six months. Those receiving phosphate showed a distinctly better appetite, and drank more water than the others, but their greater increase in weight was insignificant. When slaughtered the only difference between the two lots was a slightly larger weight of stomach, intestines, and lungs, in the case of the lambs receiving phosphate. Five bones of two lambs in each lot were carefully examined. The fresh bones of the lambs fed with phosphate were on an average slightly the heavier; they had a mean specific gravity of 1·384, the specific gravity of the other lot being 1·350. Analysis showed that there was generally more water and less fat in the bones of the lambs fed with phosphate, the dry bones of these lambs also generally contained a slightly larger proportion of incombustible matter; but looking at the absolute quantities found in the bones of the two lots, there was no increase of incombustible matter by feeding with phosphate, but a small increase of phosphoric acid, coupled with a diminution of lime. The amount of fat in most of the bones was very high, reaching to 40 per cent. in the dry bone of the fore leg.

Experiments were made as to the digestibility of phosphates. The lambs fed on hay and potatoes (chiefly the latter) digested during six days 25·8 per cent. of the phosphoric acid, and 46·0 per cent. of the lime contained in their food; and in another experiment of four days, 40·9 per cent. phosphoric acid, and 20·6 per cent. of lime. In a further experiment of six days, with two-year-old sheep, on a similar diet, 43·3 per cent. of the phosphoric acid, and 43·0 per cent. of the lime in the food were digested. When the lambs received 6 grams of precipitated phosphate per day, the whole of the extra phosphoric acid was taken up, but when the quantity was increased to 9 grams, only about half the phosphoric acid was digested. In no case was all the lime of the phosphate taken up, but a greater proportion of the lime was taken up from the larger dose of phosphate. The old sheep received superphosphate. When 10 grams were administered per day, the whole of the soluble phosphate was digested; but when the dose was increased to 20 grams, only 64 per cent. of the soluble phosphate was digested. As with the lambs, a greater proportion of lime was taken up from the larger dose of phosphate.

R. W.

The Breathing of Frogs. By W. Müller (Deut. Chem. Ges. Ber., vi, 709—710).

The author has compared the amount of oxygen consumed by two species of frogs, the green edible frog, *Rana esculentu*, and the ordinary brown frog, *R. temporaria*, in order to ascertain whether the amount of oxygen consumed by the more voracious species was not the greater. Care was taken in comparing individuals of the two species, that they should be of about the same age, and that they were caught after a continuance of fine weather. The results obtained were as follows:—

1. Single observations often vary greatly, but a series gives results in the same direction.

2. The brown frog consumes more oxygen than the green frog.

3. When hungry they consume less oxygen, but there is still the same difference between the two species.

4. In winter time under water they consume the same amount of oxygen as when breathing air.

5. Frogs frozen in ice for eight hours, breathed at the normal rate after being released.

In order to compare these results with one of the mammalia of about the same weight, the author determined the amount of oxygen consumed by the common mouse, *Mus musculus*, and found it to be more than 24 times as great as that of the frog.

C. E. G.

Experimental Researches on the Physiological Action of Nitrogen Monoxide. By F. Jolyet and T. Blanche (Compt. rend., lxxvii, 59—61).

The authors find that seeds are incapable of germinating in an atmosphere of pure nitrogen monoxide, and that even when the process has commenced it is completely arrested when the seeds are surrounded by the pure gas. In both cases the introduction of a small quantity of oxygen was sufficient to re-establish the process. Animals in all cases speedily die in the pure gas. When supplied with a mixture of oxygen and monoxide of nitrogen in the proportions of 18 to 21 of the former to 60 or 80 of the latter, they exhibit no signs of diminished sensibility. Animals breathing the pure gas lose sensibility only when all the symptoms of asphyxia present themselves.

The authors conclude that protoxide of nitrogen is not a true anæsthetic.

W. A. T.

Chemistry of Vegetable Physiology and Agriculture.

On the Intervention of Atmospheric Nitrogen in Vegetation. By P. P. Dehérain (Bull. Soc. Chem. [2], xix, 538—544).

It has been shown experimentally that the quantity of nitrogen contained in a series of vegetable crops is greater than that contained in

the manure employed for their cultivation, also that in a soil so manured the quantity of nitrogen increases. Moreover, the high lands, which are not manured, do not become sterile, although they must be deprived of a considerable quantity of nitrogenous matter by the cattle which pasture there in the summer. Again, the soil of forests is constantly deprived of nitrogenous matter by the growth and removal of trees without becoming sterile: from these facts it follows that the soil gains nitrogen from the atmosphere. The author first supposes that the nitrogen is converted into nitric acid by the eremacausis of vegetable matter. To confirm this hypothesis he heats glucose and ammonia, glucose and potash, and ulmic matter in sealed tubes together with a measured volume of air. A quantity of nitrogen is found to be taken up by these means, but evidently not to form nitric acid, for the quantity of nitrogen which disappears would require—to form nitric acid—considerably more oxygen than was contained in the tubes. Moreover, carbonic acid is formed in considerable quantity; no cyanogen is formed. He concludes that the nitrogen unites with hydrogen to form ammonia. The experiments were repeated at ordinary temperatures, employing decayed wood sawdust and glucose mixed with alkali and allowing the process to continue for a week or a fortnight, and in nearly every case a considerable quantity of nitrogen was absorbed. Under the supposition that the presence of oxygen—by combining with hydrogen—checks the formation of ammonia, he passed a current of pure nitrogen into heated mixtures of alkali and glucose, and found that 6·5—7·1 gr. of nitrogen was absorbed by 1 kilogr. of glucose, only 1·5 gr. of nitrogen being absorbed by the same quantity when air was passed instead. The substances when heated after the reaction emitted a strong odour of burnt horn, indicating the presence of ammoniacal compounds. In 21 experiments, at the ordinary temperature, out of about 90 c.c. of pure nitrogen 0·5—5·9 c.c. were absorbed (excepting in two cases), which gave negative results. He considers that these experiments prove,—1. That atmospheric nitrogen can, either in the cold or at the temperature of the soil, fix itself on carbonaceous matter analogous to that which is formed in vegetable decomposition; 2. That the presence of oxygen is unfavourable to this reaction.

Carbonaceous material in manure is advantageous, since,—1. It liberates hydrogen in decomposing; 2. It renders the conditions for absorption of nitrogen more favourable by removing oxygen from the air confined in the soil.

C. C.

Influence of the Smoke from the Freiberg Works upon the neighbouring Vegetation and the Health of Domestic Animals. By Dr. FRECTAG (Dingl. Polyt. J., ccviii, 235).

1. SULPHUROUS, sulphuric, and arsenic acids and zinc salts contained in the smoke and fumes condense with the dew on the leaves, or come in contact with the bedewed leaves; and on evaporation of the moisture a more concentrated corrosive residue is left, which quickly decomposes and kills those leaves, and so vegetation is rapidly extinguished.

Chemical analysis and observations of the appearance of the vegetation readily detect the presence and effect of these deleterious substances. Poisoning of the soil or of the entire plant is out of the question.

The metallic oxides and salts adhering to the leaves of the fodder may be dangerous to animal organisms, in causing inflammations and corrosion of the mucous membrane of the digestive organs, and under very unfavourable circumstances even death itself. This fact may always be established by dissection and chemical analysis.

W. S.

A New Beech-blight.

By J. König (Landw. Versuchs-Stationen, xvi, 198—200).

In Westphalia the beech trees have been recently attacked by a new form of blight, which, commencing on the bark, finally covers the tree with a snow-white down, producing sickness, and sometimes death. The microscope shows this blight to consist of fine threads, among which occurs a small insect, apparently an undescribed species. These threads, which are secreted by the insect, consist of wax, which has a melting point of 78°—80°, and the percentage composition of which is, carbon 81·39, hydrogen 13·58, oxygen 5·03. Both composition and melting point are very near to those of Chinese wax. The wax was in part saponified by potash. The soap shaken with ether yielded a substance melting at 49°—51·5°, solidifying at 50°—48°, and containing carbon 76·21, hydrogen 12·24, oxygen 11·55. From the soap an acid was obtained, melting at 51·53°, and solidifying at 50°—49°, the composition of which was, carbon 77·88, hydrogen 12·31, oxygen 9 81. The unsaponified portion melted at 140°—145°, and must clearly have been rich in carbon. Want of material prevented further investigation.

R. W.

Digestibility of Lucern in the Fresh State and as Hay.

By G. Kühn, A. Haase, and H. Bäsecke (Landw. Versuchs-Stationen, xvi, 81—125).

This paper is a detailed account of a carefully conducted experiment on the feeding value of lucern on two oxen. During the first period of the experiment for 13 days the animals received daily 50 kilograms of green lucern, and during the second period for the same time a quantity of hay (which had been made daily from the same portion of lucern as that given in the fresh state), containing the same amount of dry matter as did the quantity of green lucern eaten by them on the corresponding day of the first period.

Analyses of the food in both the green state and as hay at four intervals during each period are given, showing no material difference in the two states; also analyses of the food residues and of the dung, the temperature of the stall, the live weight, and the quantity of water drunk by each ox are given. The following are the percentages of the constituents of the lucern digested in each period:—

	Green lucern.			Lucern hay.		
	Ox I.	Ox II.	Mean.	Ox I.	Ox II.	Mean.
Total dry matter	64·3	63·7	64·0	60·0	58·1	59·1
Organic substances	67·4	66 6	67·0	62·2	60·4	61·3
Albuminoids	81·7	80·7	81·2	79·1	77·7	78·4
Non-nitrogenous extract.	76·9	75 0	76 0	72·0	69·2	70·6
Crude fibre............	45·1	44·1	44 6	39·3	38·5	38·9

The differences between the digestibility in the two states, though uniformly in favour of the green lucern, are not greater than is found in experiments with the same food on the same animal at different times. It is seen from the examination and analyses of the food residues that the animals when fed on green lucern selected the tenderer parts of the plant and rejected the coarse portions, which they were unable to do to the same extent during the second period when the hay was given in the form of chaff; thus, during the green feeding, the food eaten was 1 per cent. poorer in fibre and ·4 per cent. richer in albuminoids than the food given, whilst in the hay feeding there was scarcely any difference in the composition of the food given and eaten; also a slight unavoidable loss of the tenderer parts occurs in converting the lucern into hay.

From these experiments the authors arrive at the same conclusion, as from their previous experiments on red clover (*Landw. Versuchs-Stationen*, xi, 177), that the digestibility of green food is not materially altered by drying. This conclusion is confirmed by H. Weiske's experiments with lucern on sheep (*Beiträge zur Frage über Weidewirthschaft und Stallfütterung*, &c., Breslau, 1871), in which the differences in digestibility in the two states are even less than in these experiments and sometimes in favour of the hay.

The ratio between the dry matter of the food and the total amount of water taken, both in the food and as drinking water in both periods, was exactly the same, viz., ox I 3·8, and ox II 3·9 of water to 1 of dry food.

E. K.

Chemical Examination of the Bark of the Azadirachta indica

By J. Broughton (Pharm. J. Trans. [3], iii, 992).

The use of the bark of the *Azadirachta indica*, commonly called the Nim tree, is quite general throughout India as a tonic and febrifuge. It is generally used in the form of a decoction, though sometimes as a powder, and certain English authorities have stated that it has the same febrifuge qualities as cinchona bark. The taste of the bark is intensely bitter, that of the inner layer especially so. The leaves have also a very bitter taste, and are used externally as a poultice, being said to have a powerful effect in preventing glandular tumours from coming to maturity. The seeds yield a considerable amount of oil, which also has a strong, bitter taste, and is used in medicine, and for

lamps. The roots are said to have vermifuge properties, but the main virtues of the tree reside in the bark.

The bitter principle is a neutral resin, having scarcely any definite reactions. It may be obtained by exhausting the bark with alcohol of 60 per cent., precipitating the filtered tincture with water, and purifying the precipitate by solution successively in benzol, carbon sulphide, dry ether, and, finally, absolute alcohol. It is soluble in strong, boiling solutions of the fixed alkalis, from which acids reprecipitate it apparently altered. The determination of its true chemical formula was a matter of great difficulty, owing to its refusal to combine with other substances in a definite manner. It was finally determined by the discovery of a nitro-compound, which yielded a silver salt, not, however, crystalline. This nitro-compound is formed in the usual manner by nitric acid and precipitation with water, and has the formula $C_{36}H_{46}(NO_2)_4O_{11}$. The formula ascribed to the bitter principle is therefore $C_{36}H_{50}O_{11}$.

The leaves contain a small amount of bitter substance of a similar nature, but far more soluble in water. This substance, which is also contained in the bark, has very similar properties to the resin, of which it is a hydrate.

J. B.

Analytical Chemistry.

A new method of Testing with Bunsen's Flame. By Charles Huson (Chemical News, xxvii, 250).

A small double loop is made at the extremity of a thin platinum wire; the loop is dipped in moistened cream of tartar, and the latter carefully carbonised by holding it for a few seconds in the Bunsen flame. The porous mass is dipped into a solution of the substance to be tested, or if the substance be solid, a small portion is attached to it, and then inserted into the upper reducing flame.

If the metal be reducible, small metallic grains will be visible upon careful examination; but if volatile, a mirror will be readily obtained by holding a small evaporating basin, half-filled with water, just above and almost in contact with the carbon extremity. In testing for a volatile metal, the deposition of soot must be carefully avoided, but the gases resulting from imperfectly-burned tartar are advantageous in the case of non-volatile substances.

Some test-experiments are quoted, from which it appears that quantities so small as 0·000075 gram of As, 0·00013 Cu, 0·00008 Ag, are capable of being detected by the above method of operating.

J. W.

A new mode of Filtration. By Isaac B. Cooke (Chem. News, xxvii, 261).

A 300 c.c. flask is fitted with a perforated india-rubber stopper, through which a narrow glass tube of about 6 inches in length is

passed for a distance of one inch. The lower end of the tube is drawn out to a fine point, and the other is slightly enlarged in form of a funnel. Into this funnel-shaped mouth a small quantity of cotton-wool is gently packed for about half an inch, and the remainder of the wool is left outside in the form of a spreading brush. To utilise this arrangement, some water is poured into the flask, and the air expelled from the latter by steady ebullition; the stopper is inserted at the right moment, and, when condensation begins, the flask is inverted and the tube with its brush of cotton-wool plunged into the liquid to be filtered, the latter being contained in a small porcelain dish of about $2\frac{1}{2}$ inches in diameter. When nearly all the liquid has been drawn up, a stream of distilled water may be directed upon the precipitate to wash it, and the washing can be repeated as often as necessary. The cotton plug is subsequently removed by forceps over the evaporating basin, and the end of the tube having been cleansed from adhering precipitate, the basin with its contents is dried over a lamp, ignited, and weighed.

J. W.

The Alkalinity or Acidity of certain Salts and Minerals, as indicated by their Reaction with Test-paper. By W. Skey (Chem. News, xxvii, 221).

It is considered that since the carbonates, borates, silicates, phosphates, and arsenates of the alkalis possess an alkaline reaction, and since the alkaline sulphates and the corresponding sulphates of magnesia, silver, lead, and the alkaline earths, have the common character of neutrality, therefore the carbonates, borates, silicates, phosphates, &c., of the alkaline earths should show a degree of alkalinity, approximating at least to that of the corresponding alkaline salt. On direct examination with carefully-prepared litmus paper, the author has decided that all the above-mentioned salts are *alkaline;* that aluminium phosphate (wavellite), zinc phosphate, ferrous and ferric phosphate, and zinc arsenite are *acid* to test paper, and that clay and clay-slate are *neutral.* He considers that the more powerfully alkaline reactions of potash and soda are due to the much greater rapidity with which they dissolve in water, whereby they are enabled to act with greater facility, and to effect more in a given time; that the term alkalinity is improperly used to denote energy or speed of action rather than absolute potentiality, and has been, unconsciously perhaps, perverted from its true meaning to denote a certain degree of solubility—a quality which, as far as we know, may not be in any way related to it.

J. W.

Estimation of Oxygen in Vitriol Chamber-gases. By F. Bode (Dingl. polyt. J., cviii, 222—225).

It is proposed by the author that the oxygen contained in the stream of gases issuing from the Gay-Lussac's absorbing column, at the termination of the sulphuric acid chambers, be estimated by means of a solution of potassium pyrogallate, any nitrogen oxide compounds being

previously removed by potash solution; otherwise they are absorbed by the pyrogallate and more or less vitiate the results obtained.

Cl. Winkler's gas burette, or Max Liebig's apparatus, are recommended as the best to employ in the determination.

In the course of the paper it is stated that 9 per cent. Chile saltpetre on the sulphur burnt, is considered a somewhat high proportion in the German works; also that on the average about two-thirds of the nitrous gases are availably re-absorbed in the Gay-Lussac towers. It is also recommended that the gas sample taken be shaken with a little strong sulphuric acid before measuring, so as to remove any nitrous compounds.

W. S.

Detection of Sulphur by the Blowpipe. By B. Tollens (Deut. Chem. Ges. Ber., vi, 593).

When a soda bead is heated for one minute in the inner flame of a blowpipe fed with common coal gas, sufficient sulphur is communicated to the soda to produce a stain on silver. Consequently an oil or candle flame should be used in testing for sulphur by this method.

T. B.

Estimation of Phosphoric Acid in Baker Island Guano, and in other similar Guanos. By C. Gilbert (Zeitschr. Anal. Chem., xii, 1—14).

In the ordinary method of estimating phosphoric acid by means of magnesium or uranium salts, it is absolutely necessary that the acid should be present in the tribasic state. Such is the case in the Baker Island guano, but the base seldom consists of calcium alone, magnesium and hydrogen frequently forming part of it. Again, it is usual to prepare the solution of the substance for analysis by first igniting and then dissolving the ash in nitric acid. But during ignition some of the neutral (calcium-hydrogen) phosphate is converted into pyrophosphate and this is not always completely reconverted into orthophosphate by the action of the nitric acid, even with the help of heat.

To avoid these sources of error, the author proposes a plan of which the chief points are to ignite the substance with four times its weight of a mixture of 2 pts. of dried sodium carbonate, and 1 pt. of potassium chlorate, or in some cases potassium nitrate: to dissolve the mass obtained in nitric acid, and then to run into a measured quantity so much of a standard solution of uranium acetate that the reaction with potassium ferrocyanide remains distinctly visible after heating for some time on the water-bath. The solution is then titrated back by means of an equivalent phosphate solution (sodium-ammonium phosphate is preferred).

The value of the uranium solution should be determined by calcium phosphate.

If instead of the method with uranium, the original solution is precipitated with magnesia mixture, care should be taken to use a mixture prepared from the chloride, because when magnesium sulphate is used,

some of it is carried down with the ammonio-magnesium phosphate, and cannot be removed from it even by repeated washing.

A number of analyses are given to show the superiority of the author's method, and letters in its favour are added from Fresenius, &c.

G. T. A.

Determination of the Total Nitrogen in Manures.

By H. PELLET (Compt. rend., lxxvi, 1487).

IN order to obtain the total nitrogen from manures containing nitrates, the author mixes 1—2 grams of the manure with 8—10 grams of pure starch, and an equal weight of soda-lime, and makes a combustion in the ordinary way in a tube 80 cm. long, having calcium oxalate at the closed end. The action on the nitrates is apparently imperfect, as the method is said to give low results with pure nitrates. Compare *Chem. News*, xxv, 205.

R. W.

Improvements in the Mode of Estimating Ammonia by the Nessler Test.

By SIDNEY HARVEY (Chem. News, xxvii, 262).

INSTEAD of the glass cylinders which are commonly employed for the comparison of the depth of colour produced in ammoniacal liquids by the Nessler reagent, the author uses two white glass tubes, about 12 inches in length, which he adjusts upon a frame, over a small mirror in a manner frequently adopted in this method of testing. The improvement alluded to is as follows. The two tubes, A and B, are graduated throughout their length. Into A is poured, from a measuring flask, a portion of the distillate to which Nessler has been added. Into B, an equal quantity of the standard trial-liquid to which Nessler has likewise been added.

Should the colours of the liquids in the tubes not agree in tint, the height of the column of deepest-tinted liquid is to be lowered, by decanting a portion of it until the tints of colour exactly coincide. The heights of the columns of liquid are now read off.

Let $a =$ the height in millimeters of liquid in tube A; $b =$ the height in tube B; and $c =$ number of c.c. of standard ammonia used in making the trial-solution; the quantity of the latter in c.c. which should be used for the next trial-solution is expressed by the formula, $c + \frac{b}{a}$.

J. W.

Spectra of some Cobalt-compounds in Blowpipe Chemistry.

By CHARLES HORNER (Chem. News, xxvii, 241).

THE spectra of cobalt beads, and of some infusible substances which become coloured on the application of cobalt oxide, are found to be in many cases sufficiently definite and uniform in appearance, to enable

the substance to be detected by means of its spectrum, when the latter is examined with the aid of the microspectroscope.

Nine diagrams are given representing the appearance of the spectra of cobalt in different solvents. Nos. 1, 2 and 3. Cobalt oxide dissolved in boric acid, to which sodium carbonate was gradually added until the solvent had the composition of ordinary borax. 4 and 5. Spectra of magnesia, and lime when moistened respectively with solution of cobalt. 6. Spectrum of the bright blue compound of alumina; this spectrum consists of three bands, which, though frequently faint, are invariably clear and well defined. No. 7 represents the spectrum of the green compound of zinc oxide with cobalt, known in commerce as Rinman's green.

When a soda bead is formed with only a trace of boric acid, and fused with a little cobalt in the inner flame, it crystallises on cooling, and assumes a pale pink colour. An accompanying diagram depicts the peculiar spectrum of this pink bead.

The numerical values of the absorption-bands are also given.

J. W.

Determination of Ferric Oxide by Sodium Thiosulphate.

By J. M. CRAFTS (Bull. Soc. Chim. [2], xx, 50—57).

RECOMMENDS titration with sodium thiosulphate ("hypo") in a hydrochloric acid solution, from which the excess of acid has been removed by evaporating till the crust of ferric chloride begins to dissolve with difficulty. Partial neutralisation with sodium carbonate is not so suitable. Water is then added till the solution is not stronger than $\frac{1}{20}$th normal (2·8 grams Fe per litre). Stronger solutions give rather low results, but dilution with more water does not seem to be injurious. The water used for dilution need *not* be deprived of atmospheric oxygen, as the author has ascertained that the ferrous chloride produced by the reaction with thiosulphate resists almost perfectly the oxidising action of the air. About the same excess (20 p.c.) of "hypo" should be added in all determinations, and 5—6 minutes allowed for the reduction to proceed. The excess is determined with starch and iodine as usual. Nothing is said respecting the temperature at which the titration should take place, nor is addition of sodium acetate mentioned. The test analyses communicated are very satisfactory.

M. J. S.

Testing Aluminium Sulphate. (Dingl. polyt. J., ccviii, 235).

ALUMINIUM sulphate often contains excess of sulphuric acid, whereby its usefulness in dyeing is limited. The pulverised salt is treated with alcohol, whereby the excess of acid is readily removed, the salt itself remaining insoluble. The alcohol is then tested with litmus paper, and if acid be present, it can be estimated volumetrically. Pure aluminium sulphate gives, in solution with a logwood decoction, a dark violet colour, but becomes brown in presence of acid.

W. S.

Volumetric Estimation of Chloral. By V. MEYER and H. HAFFTER (Deut. Chem Ges. Ber., vi, 600—601).

WHEN chloral hydrate is agitated with excess of normal sodium hydrate solution, it is entirely decomposed, 165·5 grams of chloral hydrate neutralising 1,000 c.c. of the soda solution. By back-titration with standard acid it is of course easy to ascertain how much of the soda has been neutralised, and thence the purity of the sample of chloral. Decinormal soda-solution does not decompose chloral hydrate with sufficient readiness to make the use of it available.

This process gave satisfactory results.

T. B.

On the Detection of Grape-sugar in Presence of Dextrin and other Allied Bodies. By C. BARFOED (Zeitschr. anal. Chem., xii, 27—32).

1. A SOLUTION of grape-sugar, mixed with one of neutral copper acetate, gives at the ordinary temperature, and especially on standing, a red precipitate of reduced cuprous oxide. A solution of pure dextrin will remain several days clear and unchanged at the same temperature, but on boiling a slight reduction takes place.

2. If the solution of neutral copper acetate be mixed with a small amount of free acetic acid, grape-sugar is reduced, after a moment's boiling and subsequent rest, whilst dextrin is not.

Excess of acid must be avoided. The solution is best made by dissolving 1 pt. of crystallised neutral copper acetate in 15 pts. of water, and adding to 200 c.c. of this liquid 5 c.c. of acetic acid (containing 38 per cent. of anhydrous acid). The above methods, and more particularly the second, serve also for the detection of grape-sugar in presence of gum, cane-sugar, and milk-sugar, but the last substance must be somewhat dilute.

With regard to the ordinary tests the author speaks as follows:—A solution of dextrin gives with copper sulphate and caustic soda a clear blue liquid, which remains unchanged at the ordinary temperature, if it contains only a small amount of dextrin (*e.g.*, 1 per cent.), but if somewhat concentrated, a red precipitate of cuprous oxide begins to separate in the course of a few hours, and continues to increase till the liquid has reached a certain point of dilution. If heated to boiling, the mixture gives immediately, or very soon, a reddish-yellow or red precipitate.

Fehling's solution produces the same results, but acts more quickly and in more dilute solutions of dextrin.

The results of a number of experiments are given in which solutions of dextrin, more or less concentrated, were tested with copper sulphate and caustic soda, and with Fehling's liquid. They were left at rest for periods varying from 24 to 168 hours, and at the end of each period the liquid was poured off from the precipitate and again left at rest.

Reduction took place most strongly at first and in the more concentrated solutions. In very weak solutions, little or no reaction was seen.

G. T. A.

Estimation of Sugar by Barreswil's Method.
By M. LOISEAU (Compt. rend., lxxvi, 1602—1605).

THE author discusses the influence exercised on the determination of glucose by this method by the amount of soda employed. He finds that an error is involved on account of the circumstance that an excess of soda favours the recoloration of the decolorised Fehling's solution, so that when the experiment is rapidly performed, less sugar is required to decolorise it than when the operation is carried out slowly. Thus 2 c.c. of cupro-potassic solution, diluted with 50 c.c. of a soda solution containing 75 grams per litre, were not entirely decolorised by 40 c.c. of an inverted sugar solution (containing 1 gram per litre) slowly added, whereas 12 c.c. of the same solution removed the colour when quickly added. The influence thus exercised by time may be almost entirely neutralised by diluting the cupro-potassic solution; it must not be too dilute, however, or the decoloration is greatly retarded.

H. E. A.

Estimation of Alcohol in Fusel Oil. By G. L. ALEX (Arch. Pharm. [3], ii, 289—300).

FUSEL oil containing less than 15 per cent. of proof spirit is free from duty in England. The author was requested to examine a sample, and found it to contain less than 10 per cent. of proof spirit, but the Custom House authorities in London asserted that it contained no less than 44 per cent.;* and the object of the present paper is to show that the examination at the Custom-house is founded on a false principle. A certain quantity of fusel oil is mixed with an equal volume of water, and after shaking allowed to stand for twelve hours. At the end of this time the liquid has separated into two layers, the upper one being fusel oil and the lower one spirituous water. From the specific gravity of the lower layer the percentage of alcohol and the duty are determined. This method, founded on the insolubility of fusel oil in water, would answer very well if it were not that crude fusel oil is a mixture, according to circumstances, of amyl alcohol, with ethyl, propyl, and butyl alcohols. The last two being likewise soluble in water, are thus reckoned by the Custom-house method, together with the ethyl alcohol, as proof spirit. From his experiments, of which a detailed account is given, the author concludes that the best method of estimating alcohol in fusel oil for commercial purposes is to distil off from 100 c. c. of the sample to be tested, about 5 c.c., and to shake this up with a saturated solution of common salt; if, on standing, half the mixture or more separates as fusel oil, there is certainly under 15 per cent. of proof spirit present.

G. T. A.

* The author does not appear, however, to know the exact meaning of the term "proof spirit," since he puts in a note: "Proof spirit = probehaltigen, neuen spiritus."—ED.

Analysis of Glycerin. By P. Champion and H. Pellet (Bull. Soc. Chim. [2], xix, 494).

Commercial glycerin frequently contains glyceric ethers, volatile fatty acids, and other undetermined bodies. The action of nitro-sulphuric acid on these impurities is to convert them into bodies which are soluble in water, while the glycerin is transformed into nitroglycerin, which is insoluble. The nitroglycerin is washed first with a dilute solution of caustic soda, afterwards with water, and subsequently dried in a water-bath. Before being dried it is mixed with its own bulk of wood-spirit to assist in the volatilisation of the water present. From the weight of nitroglycerin found may be calculated the amount of pure glycerin present in the sample. The authors found that 100 grams of glycerin chemically pure, and concentrated at 120°—150° *in vacuo*, yielded 190 grams of pure nitroglycerin. The theoretical yield is 247. Careful attention to the strength of acid used, the temperature, and all other details are necessary to ensure constant results.

J. B.

Estimation of Nitroglycerin in Dynamite. By P. Champion and H. Pellet (Bull. Soc. Chim. [2], xix, 496).

Dynamite may be classed in two distinct categories according to the nature of the absorbing body.

1st. Dynamites with inert base (silica, ashes, &c.).

2nd. Dynamites with active base (*dualine*, *lithofracteur*, &c.). In this case the absorbing substances (resin, finely-powdered coal, sodium nitrate, &c.) decompose during the explosion of the nitroglycerin, furnishing gaseous compounds which increase the active power of the dynamite.

1. *Dynamite with Inert Base.*—Exhaust the dynamite with wood-spirit under heat, and evaporate the solution in a water-bath until it ceases to lose weight.

2. *Dynamite with Active Base.*—Treat first with boiling water, which dissolves nitrates and causes the resin to float on the surface. Remove the resin, and separate then the nitroglycerin by wood-spirit, and evaporate the solution in the water-bath.

J. B.

Improvements in Toxicological Investigations. By F. Selmi (Gazz. Chim. Italiana, ii., 544—551, 583—588. Abstracted from the Memoirs of the Bologna Academy of Sciences [3], vol. I.)

I. *Detection of Arsenic.*—The author asserts that the ordinary methods for the detection of arsenic in cases of poisoning do not yield the whole of the arsenic present, and that sometimes they fail to give any indication of arsenic whatever, though it be present, *e.g.*, when Reinsch's test is applied to a mixture containing the sulphide. He proceeds as follows:—The organic substance suspected to contain arsenic is introduced into a retort with a little water, and monohydrated sulphuric acid is then added, elevation of temperature being avoided.

To the retort is fitted a tubulated receiver, and to this two Woulfe's bottles containing water. A current of hydrochloric acid gas is passed through the organic mixture, the retort and receiver being placed in an oil-bath, as soon as the reaction becomes quiet, and kept at 105°—110°. If the temperature rises above this point, sulphurous acid is formed. The arsenious chloride in the bottles is precipitated by sulphuretted hydrogen. By this method the author detected arsenic in mud containing $\frac{1}{100,000}$ of its weight of that metal, whether it was in the state of arsenious or arsenic acid, or of the sulphide. Antimony compounds do not interfere with the reaction. (There is nothing new in the principle of this process, nor does it appear how this particular application of it overcomes the difficulty, *e.g.*, of decomposing the sulphide.) Instead of causing the suspended sulphide to agglutinate, after precipitation, by heating, the author adds some carbon sulphide, and agitates the liquid. After standing at rest, the globules of carbon sulphide at the bottom are found enveloped by a pellicle of arsenious sulphide. On pouring off the liquor and leaving the residue exposed to the air, the carbon sulphide evaporates, and leaves the arsenious sulphide, which is then treated by the usual methods. Its conversion into arsenic acid is very easily effected by boiling it in sulphuric acid, mixed with a little water and nitric acid. In oxidizing the arsenic mirror, the author adapts a bulb-tube containing alkali to the oxidizing tube, and draws air through the apparatus. In burning the arsenetted hydrogen he uses the following modification of Flaudin and Danger's apparatus. The flame is introduced as usual into the small chimney, to which is fitted a tubulated flask, carrying in the tubulure a long glass tube. A stream of cold water flows over the tube and flask, which then condenses the arsenious acid.

II. *Detection of any Metal in Organic Mixtures.*—The liquid left in the retort after arsenic has been volatilised is evaporated to one-half, sodium carbonate is then added to strong alkaline reaction, and evaporation carried to dryness. After 15 per cent. of sulphur has been added, the whole is brought to a red heat in a long-necked glass crucible, coated with clay, and enclosed in an assay crucible. Mercury and a part of the tin present will then be sublimed as sulphides upon the neck of the vessel, while other metals and the rest of the tin will remain behind as sulphides.

III. *Detection of Phosphorus.*—Mitscherlich's method is modified thus:—The substance is placed in a large flask; this is followed by a flask half as large, and this by a test-tube containing a layer of carbon sulphide and a layer of water. The delivery-tube which dips into the test-tube is separated from the carbon sulphide by a space of a few millimeters. The air is first driven out of the apparatus by a current of carbon dioxide. The contents of the first flask are then boiled, till one-third has passed over into the second flask, which is cooled. If the distillate contains no alcohol, ether, or oil of turpentine, it will evolve an odour of garlic, a phosphorescent cloud being at the same time produced, if phosphorus be present, on shaking the flask in a dark place. As a confirmation, the carbon sulphide and water in the test-tube is poured into the receiver, a little sulphur is added, and, after agitation, the carbon sulphide is allowed to settle. The water is sepa-

rated, and the carbon sulphide gently evaporated, till the phosphorescence appears. If alcohol or ether be present, the carbon sulphide must be washed several times by decantation with water. If oil of turpentine be present in not very large quantities, the carbon sulphide is shaken with a little concentrated sulphuric acid, which removes the oil of turpentine. By evaporating a little of the sulphide and observing whether the sulphur previously added crystallises in a state of purity, it may be ascertained whether the oil of turpentine has been entirely removed. When the amount of the oil present is large, the substance is treated as usual with carbon sulphide, the latter is washed with water, and a known volume of it evaporated. The weight of the residual oil of turpentine having been noted, a mixture is made of the oil and recently distilled carbon sulphide in the same proportions. To each solution a little solution of iodine in carbon sulphide is added. Both liquids are coloured rose-red, but the colour quickly disappears in the liquid containing phosphorus. If a little iodic acid and alcohol of 98 per cent. be also added, the liquid containing no phosphorus assumes a rose-violet colour, while the solution containing phosphorus becomes yellowish, and finally colourless. If, however, the vessel is shaken before the yellow colour of the latter solution has disappeared, the liquid becomes rose-violet, but of a paler tint than the solution without phosphorus. After standing for some time the colour changes again to yellow. This may be repeated several times.

The author subsequently found it best to dissolve out the phosphorus by digesting the substance at the ordinary temperature in alcohol of 95—98 per cent., containing 10 per cent. carbon sulphide. The supernatant liquor is agitated with fresh carbon sulphide, which is then evaporated, and the usual tests applied. He thus modifies Blondlot and Dusart's apparatus for acting with hydrogen on the precipitate produced by phosphorus in silver nitrate. The phosphoretted hydrogen is evolved and ignited at a platinum jet, which just enters a large tube leading into a bottle containing water. An aspirator being set at work, the products of combustion are condensed in the water. He finds that viscera, in putrifying, oxidise free phosphorus.

IV. *Detection of Blood by Formation of Hæmin Crystals.*—The difficulty of obtaining these crystals is largely due to the non-employment of the most favourable temperature, which the author finds to be 75°—80° in summer, and 100° in winter. He also finds that the solution of sodium chloride in acetic acid should be one fourth of saturation. When the blood is mixed with clay, no crystals can be obtained by the usual method, on account of the absorbing action of clay. If, however, the clay is treated with soda, and the latter is neutralised with hydrochloric acid, evaporated to dryness, and the residue dissolved in acetic acid, the crystals appear without difficulty.

V. *Alkaloïds existing in Alcohol.*—On treating by Stas's method, the fresh and putrid stomachs and intestines, both of persons suspected to have died by poisoning, and of those who had died a natural death, an alkaloïd was constantly detected, which, however, gave none of the specific reactions of a poisonous alkaloïd, nor those of quinine. The alcohol used was at last found to be the source of this alkaloïd. The possibility of such an event should be borne in mind in testing for the

alkaloïds. Moreover, this substance was not extracted from putrid meat by ether, but water readily dissolved it out, from which the author infers that in Stas's method the usual alkaloïds may sometimes be present, and yet not be detected.

VI. *Characteristics of Picrotoxin and Colocynth.*—*Picrotoxin* is soluble in warm acetic acid, crystallising, on cooling, in needles; it reduces cupric oxide dissolved in potash; gives a brick-red colour when evaporated to dryness with an alkali; turns ammoniacal silver nitrate brown; produces a brown pellicle on cupric acetate solution when boiled with it; colours an alkaline aqueous solution of picric acid rose-red. *Colocynth*, when evaporated with acetic acid, forms small, white, insoluble crystals; deposits a blue flocculent precipitate when boiled with cupric acetate; has no action on silver nitrate; gives white precipitates with an aqueous solution of tannin and lead iodide dissolved in sodium acetate.

B. J. G.

Experiments in the Domain of Forensic Chemistry.
By H. STRUVE (Zeitschr. Anal. Chem., xii, 14—27).

The Detection of Prussic Acid.—In a case of poisoning with potassium cyanide, prussic acid was detected in the blood and tissues, by distilling them with water and a few drops of tartaric acid, and applying to the distillate the usual Prussian blue and sulphocyanogen tests. The first gave in each case negative, the second positive results.

Experiments undertaken to show the presence or absence of sulphocyanogen as a normal constituent of the body, led to negative results, except in the case of the saliva. Traces, however, were found in one case in blood from a liver.

In another case of poisoning with potassium cyanide the examination of the tissues did not take place till eight months after death, and then no trace of prussic acid could be found, but formic acid was present, and this was considered by the analyst to be a proof of death from potassium cyanide, the formic acid being produced by the decomposition of the cyanide.

The author's experiments on the point led to results which contradicted the conclusion that the formic acid was produced by the simple decomposition of the cyanide.

Of the tests for prussic acid, the best is undoubtedly the sulphocyanogen reaction; but as both sulphocyanic acid and sulphocyanate of ammonium are volatile, a few drops of caustic potash should be added before concentrating the liquid previous to the addition of ferric chloride. The blue colour produced by prussic acid in a solution containing tincture of guaiacum and a copper salt affords a means of detecting extremely minute traces of it, but other bodies besides prussic acid give the same reaction.

G. T. A.

Testing of Shoddy. By ROBERT SCHLESINGER (Dingl. polyt. J., ccvii, 414—417).

Technical Chemistry.

Photochemical Researches on the Use of Gases as Developers, and on the Influence of Physical Condition on Sensitiveness. By M. Merget (Compt. rend., xxvi, 1470—1472).

The salts of gold, platinum, palladium, and iridium are reduced by certain gases in the presence of moisture, but not when dry. By mixing one of these salts with a substance which becomes deliquescent on exposure to light,* and using the mixture for sensitising paper, a photograph is obtained, which after developing with the reducing gas—mercury vapour, iodine, sulphuretted hydrogen, or even hydrogen containing traces of foreign gases—is fixed by simple washing with water. Such photographs are said to be indestructible by any agent which does not attack the paper. Prints have even been obtained with copper salts, but the details are not given.

Moisture affects also the condition in which the metal is precipitated on the paper. When present in sufficient quantity to produce visible wetness, it causes the metal to separate as a homogeneous, perfectly transparent film; but when the plate is nearly dry, the metal is deposited in a pulverulent condition, giving a tone more or less deep. Gold salts in particular behave in this way, and by two exposures in different hygrometric conditions can be made to yield direct positives, which do not even require washing or any subsequent process. It is also found that by mixing soluble salts of platinum, silver, &c., with insoluble powders their sensitiveness to light is greatly increased.

M. J. S.

A few Facts concerning Bleaching Powder.

By George E. Davis (Chemical News, xxvii, 225).

The analyses of, and experiments relating to the manufacture of bleaching powder detailed in this communication, tend to show that it is practically impossible to raise the active chlorine in a sample higher than 40 per cent., even by the employment of a large excess of gas: that the active and total chlorine should be identical, any predominance of the latter being due to hydrochloric acid mechanically carried over from the chlorine still. It is exceedingly disadvantageous to allow a powder to gain a considerable excess of water, either through the intervention of very moist chlorine, or otherwise, since under these circumstances a maximum of even 35 per cent. active chlorine cannot be obtained, and a sample is ranked as indifferent, when from any cause its percentage falls below this number.

The author alludes to the various formulæ which have been proposed in connection with bleaching powder, but his analyses are not of such a nature as to lend material support to any particular formula.

J. W.

* Poitevin's solution is mentioned; it appears to consist of ferric tartrate.

A Productive Source of Ammoniacal Salts. By B. TERNE (Dingl. polyt. J., ccviii, 386).

IN the neighbourhood of Chicago are the immense slaughter-houses of the American north-west. In the slaughtering season, from November to January, as many as 25,000 to 30,000 cattle are slaughtered in a single day. This number extends over about twenty establishments. A large quantity of refuse and useless flesh remains on hand, and is placed in a large iron boiler and boiled under a pressure of three to four atmospheres. The fat rises to the top, and beneath it is a liquid which might be called a solution of glue, if the continued boiling under pressure had not completely destroyed its binding power.

These tank-waters were found to contain from 105 to 118 grams per litre of gluey extractive matter. This, as already observed, is useless as glue; but the author also found that the liquid contains ammonia equal to from 5 to 8½ grams per litre of ammonium chloride.

W. S.

English Glaze for Earthenware. By H. SEGER (Dingl. polyt. J., ccviii, 234).

THE glaze is fixed on a light yellow piece of ware of great uniformity and porosity, and of a fire-proof clay. It is of a dark violet-brown colour, and somewhat translucent, of extraordinary lustre, and free from all flaws.

For analysis a piece of Burslem ware was taken, and a part was broken off where the glaze lay thickest.

The chemical analysis of this glaze gave in 100 parts by weight the following results:—

Silica	40·56
Alumina	6·07
Lead oxide	40·04
Ferric oxide	2·59
Manganese oxide	7·14
Lime	2·58
Alkalies and loss	1·02
	100·00

In order to obtain a glaze of similar composition and properties to the above, the following mixture was taken:—

Quartz or glazing sand, 28 parts, silver litharge, 40 parts, pipeclay, 18 parts, best manganese oxide, 9 parts, chalk, 5 parts.

In order to produce the uniformity and beauty of colour as in the English ware, the materials were melted into a frit first, and then ground finely. The burning of the frit can be easily accomplished in a potter's oven furnished with a cover.

W. S.

Preparation of an Enamel suitable for Frosted Glass-making.

By H. G. Benrath (Dingl. polyt. J., ccvii, 402—405).

Advantageous use of Manganese Liquors in Glass-making.

(Dingl. polyt. J., ccviii, 396.)

By first neutralising the manganese still-liquors of the bleaching powder manufacturer with powdered limestone, running off the clear liquors, and precipitating with milk of lime, a thin muddy precipitate of manganese hydrate with excess of lime is obtained. This turns brown and nearly black on the surface, on exposure to air, and when dried and calcined, yields a dark brown and nearly black oxidised product, which may be substituted for the ordinary manganese dioxide for the use of the glass maker, the lime in no wise interfering, and the product being free from iron, which is precipitated in the neutralising operation.

W. S.

Manganese, a Substitute for Nickel in German Silver.

(Chem. News, xxvii, 249.)

Upon the authority of Dr. Percy, it is stated that manganese can be substituted for nickel in the manufacture of German silver without affecting the appearance or general character of the alloy, and that although this fact has been known to some manufacturers for many years past, the manufacture of the manganese alloy has not, for commercial reasons, been proceeded with.

Mr. J. Fenwick Allen, in a paper read before the British Association in 1870, gives detailed directions for the preparation of alloys of copper and manganese, and of copper, zinc, and manganese, upon the manufacturing scale. The former alloy, when the proportion of manganese ranged from 5 to 30 per cent., was found to be both malleable, ductile, and of great tenacity; it was brittle when hot, but in the cold it rolled with ease, and was highly elastic. The zinc alloy was capable of being rolled from hot to cold, and possessed some qualities of German silver, but not the best.

The metallurgy of manganese, as developed by Mr. Hugo Tamm, has been already noticed in this Journal, vol. xxv, page 1076.

J. W.

Direct Preparation of Iron from its Ores. By P. Tunner

(Dingl. polyt. J., ccviii, 218—222).

A critical description of Siemens' rotary gas-furnace for the direct preparation of malleable iron and cast steel from iron ores, already fully described in this Journal by the inventor (pp. 661—678 of this volume).

W. S.

Obtaining Silver by Amalgamation, in Chile.

(Dingl. polyt. J., ccviii, 396.)

THE old amalgamation process is greatly improved by the use of cuprous chloride, the reaction being represented as follows:—

$$Ag_2S + Cu_2Cl_2 + Hg = Ag_2Hg + CuS + CuCl_2.$$

In this case, therefore, no mercurous chloride is produced. If the ores contain silver chloride or bromide, a quantity of lead dissolved in mercury is added, equal to 25 per cent. of the silver present. Lead chloride is then formed, and the loss of mercury amounts to only 25 per cent. of the silver, instead of 150 per cent. which used to be lost. The ores are crushed by cast-iron wheels of four tons weight. A stream of water continually carries the finely ground ore away, and it collects in troughs.

Four tons of this ore are placed in rotating vessels $1\frac{1}{2}$ meters diameter and 1·8 meters long. Into these are introduced 28 to 30 litres of cuprous chloride solution, prepared by saturating a cupric sulphate solution at 20° Baume, with common salt, and then boiling with copper turnings in wooden vessels, by steam. The solution is kept out of contact with the air. The vessels are rotated for a short time, in order to thoroughly mix the ore and solution, and a quantity of mercury is added equal to from 20 to 25 times the weight of silver contained in the ore, with further rotation. The silver amalgam is then washed out. It is contaminated with cupric sulphide and oxide. These are removed by water and solution of ammonium carbonate. The amalgam can then be subjected to distillation. If the ores do not contain over $\frac{50}{10,000}$ths of silver, the residue retains only $\frac{15}{10,000}$ to $\frac{2}{10,000}$th. This operation may be used for most ores, but not for copper pyrites, blende, and such as contain free metallic arsenic, because in these cases the loss of mercury is considerable.

W. S.

So-called Zinc-caps for Bottles, Flasks, &c.

By G. C. WITTSTEIN (Dingl. polyt. J., ccviii, 341).

THESE are so greatly contaminated with lead, that their composition in many cases would be most correctly expressed in saying that they consisted of lead containing zinc, rather than the reverse. The amounts of lead in caps covering champagne, liqueur, mustard, mineral water and beer flasks, were respectively 90·13, 91·33, 92·4, 93·1, 94·2 per cent. The danger is particularly great in the case of flasks containing liquids with free acids present, as if they are not completely emptied at once, and the cap replaced while a portion of the liquor remains, a drop or two of the slightly acid fluid is liable to come in contact therewith, and on standing to act upon the lead, bringing a portion into solution. The drop or two of lead solution on the cap is thus likely to be carried into the stomach of the next drinker from this flask. Cases of acute lead poisoning have thus been occasioned. The author has also detected lead largely present in tin-foil used to wrap cheese in.

W. S.

Action of Low Temperatures on Wines and Spirits.

By MELSENS (Compt. rend., lxxvi, 1585—1588).

WHEN cognac or rum is cooled to −30°, it can be drunk from a wooden vessel without causing any violent sensation of cold. Below −35° it becomes viscid, syrupy, and often opalescent. At −40° or −50° it solidifies, and in this state it seems to the tongue less cold than an ordinary ice. At −71°, it produces a sensation similar to that caused by a liquid just too hot to be borne, and when it is placed upon the dry skin, it causes a slight burn.

When vin ordinaire is submitted to the action of a freezing mixture, the water contained in it solidifies. The liquid portion being separated from the solid by a centrifugal strainer, the solid part is found to contain but a trace of alcohol and organic matter, and develops fungus in a very short time. By using a screw-press, 25 per cent., and in the case of Burgundy 40 per cent. of the winé may be thus separated as water. This treatment is recommended as a means of enriching poor wines, and so rendering them capable of preservation.

B. J. G.

Adulteration of Pepper. By M. BOUCHARDAT (Pharm. Jour. Trans. [3], iii, 993).

DURING the examination of a large number of samples of ground pepper, as sold in France, the author found the most common adulterant to be one prepared by drying and finely pulverising the parenchyma of potatoes which is left as a residue in the manufacture of starch. Other adulterants found were lentil flour, earthy matter, chalk and linseed cake.

J. B.

New Process in the Manufacture of Stearin.

By Professor BOCK (Dingl. polyt. J., ccviii, 230—233).

IT is known that the neutral fats consist of small globules divisible into two parts, an outer covering, in the case of the animal fats, consisting of cellular matter, gelatin, fibrin, and albumin, and in that of the vegetable, of gum, vegetable albumin and cellulose. Each globule is filled with the peculiar fat, in more or less complete development.

A small quantity of tallow dissolved in ether, does not give, properly speaking, a solution; as, microscopically examined, the liquid is found to contain the little globules floating intact therein. They are found, however, to have increased in size from 60 to 100 per cent., and the contents have become transparent, this being the effect of endosmose. After careful evaporation of the ether, the tallow is obtained again, exactly as it was before the so-called solution.

The difficulties arising from the coagulated albumin have been overcome hitherto only by empirical methods. The coagulated albumin is soluble in strong caustic alkalis, as also in water or steam, of which the temperature exceeds 160°.

By distillation and by the autoclave method, with or without the

old-fashioned lime saponification, the difficulty of the albumin is overcome by the very high temperature employed.

In the acidifying operation, very improperly called "acid saponification," no decomposition takes place. For forty years it has been imagined that a compound acid, a sulphostearic acid, was formed. After complete acidification the fat, washed with water, remains still neutral fat. After the acidification with concentrated sulphuric acid, no trace of glycerin compound is found, because the first hydrate, viz., an acid of 66° Baumé, yields no water to the glycerin requisite for the formation of glyceryl hydroxide. With the temperature considerably raised, formation of acrolein takes place during the acidification, denoting the destruction of the glyceryl.

The benefit obtained by the acidification results from the corrosion and rupturing of the albuminous cells; this is attended also with partial carbonising. Being ignorant of what actually takes place during this process, the owners of different works have used innumerable modifications of the acidifying process, in the belief that each possessed the most valuable secret for the formation of the compound acids.

Frémy's recommendation "that the action of the acid be only momentary," is a sound one, as too great excess either as to time, quantity, or temperature, leads to decomposition of the *enclosed* fat in part, as well as of the envelopes.

After the due amount of acidification, the neutral fat is, so to speak, stripped of its clothing, or *this cellular structure is* so far corroded as to give free egress to the contents. The fat is now in a condition fit for decomposition. which is accomplished after a few hours, with the acid mixture chemically necessary, 4 to $4\frac{1}{2}$ per cent., and with the required amount of water. The crystallisation and other usual signs show that the decomposition is completed.

After running off the glycerin-water, the fat acids are found more or less dark coloured. They are now distilled, when the melting point of the product is found to vary from 49° to 51°, according to the quality of the tallow employed.

The essence of the new method is in dispensing with the distillation. The object of this distilling operation with superheated steam is the removal of the black colour caused by the presence of partially carbonised albuminous cells which are suspended in the fat acids, and will not settle because their specific gravity is almost identical with that of the liquid in which they are suspended. The author overcomes this difficulty by submitting the substance to an oxidation, whereby the specific gravity of the cellular particles is raised from about 0·9 to 1·3. Thus the coloured particles are precipitated, and the fat acids are ready for being washed. The further treatment by cold and warm pressure is the same as by all other methods.

After five years' experience of this improved method, it is found that the following results are obtainable:—

From tallow, after complete decomposition, 95 per cent. of the fat acids are obtained, which lose by oxidation and washing 2 per cent. The glycerin amounts to $6\frac{3}{4}$ per cent. of the tallow at 23° Baumé, and is completely free from organic acids.

The oleic acid is in all respects like that obtained by lime saponification, but richer in concrete acids, and much sought after by soap-makers and cloth manufacturers. The stearic acid is quite similar to that furnished in the lime saponification, but much harder, and has a melting point 58° to 60°.

The stearin obtained consists of 55 to 60 per cent. of the tallow. Other advantages of this process are that it may be used in the hottest summer without danger, seeing that it is worked with steam in open vats; and the avoidance of high temperatures prevents the danger of injurious effect upon the fat acids. The wages are small and the apparatus cheap and easily repaired; the method likewise answers for vegetable as well as for animal fats, and is employed to the greatest advantage for the former when combined with distillation.

W. S.

Lubricating Oils, especially Rosin-oil.
(Dingl. polyt. J, ccviii, 237.)

"*Vulcan oil*" is the distillate of Virginian petroleum which passes over almost at the last, and has a sp. gr. from 0 870 to 0 890. This, whilst warm, is acidified with 6 per cent. of fuming sulphuric acid in a lead vat, then drawn off from the acid, and washed with water to the complete removal of the acid. The product is then mixed with 5 per cent. of rape-oil. Also that oil which distils over in the petroleum distillation after the illuminating oil (until of sp. gr. 0·860) passes over, is taken separately, until it solidifies when dropped upon a cold metal plate, and with this 5 per cent. of crude rape-oil is mixed.

Another lubricating oil from petroleum is the "opal oil." This oil, of sp. gr. 0·850 to 0·870, is acidified like "vulcan oil," and mixed with 10 per cent. of rape oil.

For parts of machinery which move with great rapidity, as railway axles, spindles, &c., lubricating oils from petroleum cannot be used. "Rosin oil," when specially purified, is far the best for this purpose. Its strong odour, as also the liability to separate rosin when warm, are removed as follows:—100 pounds of dry thick rosin-oil are heated in a pan till of thin fluidity. The fire is then removed, and three pounds of fuming sulphuric acid are gradually dropped in, with constant stirring. After a half an hour's mixing, the oil is left to stand for twelve hours, and is then drawn off by a siphon into a wooden vat. It is then washed with hot water, drawn off after twelve hours' settling, and the washing is repeated till the water runs off without acid reaction. The water is at first added hot to the oil without mixing, as long as it flows off milky. After several days' separation, a dark yellow, faintly odorous rosin-oil is obtained without blue reflection. This oil, mixed with olive or rape oils, may be used advantageously for lubricating the heavy parts of machinery.

To obtain the oil perfectly free from odour, and of clear yellow tint, the dark yellow rosin oil is run into a flask or globe, and to 100 pounds of rosin oil 1 pound of water is added. The whole is well shaken, and gradually 8 pounds of hydrochloric acid diluted with 10 pounds of water are mixed in. To this 1 pound of red lead and

5 pounds of dilute hydrochloric acid are added, and the whole is frequently shaken. After some days the oil is drawn off, washed with water till free from acid, and set in the sunlight for about eight days in a flask. Thus treated it becomes of a light yellow tint.

The yellow rosin oil when mixed with one-third rape or olive oils, yields a good lubricating oil for all machine purposes. It does not deposit rosin in the slightest. It can also be mixed with petroleum. Mixed with rape oil, it appears in the trade as an adulterant for olive oil.

W. S.

Yellow on Woollens previously Coloured with Aniline Dyes. (Dingl. polyt. J., ccviii, 238.)

The aniline colours are, as is known, destroyed and reduced by zinc dust, whereas the so-called "xanthine" resists the reducing action. Thus it is possible to print woollen fabrics yellow which are previously coloured with aniline tints. The following mixture and process are recommended for the purpose:—

40 grams xanthine are dissolved in 50 grams of water; also 250 grams of zinc-dust are stirred up in 500 grams of water; 30 grams of sodium bisulphite are dissolved therein; and both solutions are mixed.

After the printing the goods are wrapped up in paper and damped.

W. S.

Dyeing of Felt with Aniline Colours. (Dingl. polyt. J., ccviii, 239.)

For the dyeing of felt hats, aniline colours can be used in every case. The colouring matter is used repeatedly to make the tint satisfactory. If the dyeing follows the fulling the felt is not penetrated so easily, but the hair can be directly dyed and the dyed hair fulled. For this purpose a solution of the dye is made in boiling water, then allowed to cool, and filtered. A pan with water heated to 30° is prepared, and into this the necessary quantity of dye is introduced, stirred up, and the hair moistened, and enclosed in a basket is placed in the bath. The bath is repeatedly heated to 60°, and the basket agitated therein continually. Fresh colouring matter is introduced when the hair has absorbed a certain amount, the basket being for the instant removed.

When the hair is fully dyed the basket is removed and the hair allowed to cool, and it is then well rinsed. Mixtures of aniline colours may be used for particular tints with good effect.

For *brown* the bye-products from fuchsine are employed, which are known in the trade as "cerise," "merron," &c. These give with indigo-carmine and picric acid, with addition of a little sulphuric acid, splendid brown shades. For the preparation of the favourite "Bismark" a solution of Manchester brown can be used, which is toned down by addition of indigo-carmine, picric acid, and fuchsine.

W. S.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

XLVI.—*On the Optical Properties of some Modifications of the Cinchona Alkaloïds.*

By David Howard.

The remarkable optical properties of the cinchona alkaloids, first noticed by Bouchardat in the *Annales de Chimie et de Physique* [3], ix, 213, have since received much attention from Pasteur and others. More recently Dr. de Vrij has endeavoured to utilise them in the analysis of the cinchona barks; and in the course of the present year Dr. Oudemans, in a paper in the *Ann. Chem. Pharm.*, clxvi, 65, and Dr. Hesse, in the same Journal, clxvi, 217, have added greatly to our knowledge of the subject.

It is, however, yet far from complete; in fact, the two last-mentioned papers rather indicate than exhaust two elements of special interest and difficulty in the study. The results of Dr. Oudemans' unexpected discovery of the influence of solvents without chemical action on the alkaloids, and of Dr. Hesse's observations on the very great and often anomalous alterations in the specific rotatory power of the alkaloids, caused by variations in the proportion of acids present in solutions of the salts, demands the careful attention of all students of the optical properties of these bodies.

There is one branch of the subject which has not been much studied, except in the case of quinicine and cinchonicine, namely, the influence of modifications in the molecular structure of the alkaloids on their specific rotatory power, and I now propose to give the results of my observations on some of the cases which offer themselves for examination.

The degree of modification that the molecule can suffer without losing its distinctive optical properties seems to be but slight; where a radical change has taken place, the power of deviating the polarised ray is lost. The quinoline series, for example, are without that power.

The remarkable change in the optical properties of the alkaloïds in the formation of quinicine and cinchonicine was, as is well known, discovered by Pasteur, and in a paper I read in January, 1872, I gave determinations of the deviation of the yellow ray by these alkaloids and their salts.

I did not then notice an approximate relation which those numbers

bear to those given by the alkaloïds from which they are derived, which is at any rate near enough to suggest an analogy to the change produced in tartaric acid by heat, from which at first sight it differs. In the case of tartaric acid, bodies of similar rotatory power but opposite in direction give inactive bodies without that power. With the alkaloïds the case is different. The pair of isomerides possess opposite rotatory powers of very different intensity, and the result of the change is a substance still possessing the same power, but in a slighter degree; but it is curious to see how nearly that degree approaches to the mean between the two extreme rotations.

The *latest published determinations* are those of Dr. Hesse, which bear the marks of his usual accuracy. He gives for quinine in alcoholic solution a specific rotatory power of 166°↖, and for quinidine of ↗260°. The mean of these is ↗47°. The rotatory power of hydrate of quinicine in similar circumstances is ↗39°. It is not easy to determine the exact degree of hydration of quinicine, as it is very intolerant of heat, and discolours before losing all the combined water, but experiments show that it approximates closely to one atom, *i.e.*, 5·26 per cent. Allowing for this, the rotatory power of an anhydrous quinicine will be ↗41°. Moreover, the effect of sulphuric acid in all the four principal cinchona alkaloïds is to increase the deviation of the ray. With quinicine it is the reverse. The specific rotatory power of oxalate of quinicine in solution in water containing an equivalent proportion of sulphuric acid is ↗14°, which equals ↗19·4° for the contained quinicine. Dr. Hesse gives, as the result of his experiments on quinine in solution as sulphate in alcohol, a deviation of 220°↖, and on quinidine of ↗261°, the mean of which is ↗20·5°.

A similar approximation is found to be the case with cinchonicine; the rotatory power of cinchonidine is 112°↖, of cinchonine, ↗226°, the mean being ↗57°, that of hydrate of cinchonicine is ↗48°, which makes that of anhydrous cinchonicine ↗50·5, the hydration being in this case also one atom. The sulphate does not agree so well. Dr. Hesse gives for cinchonidine in solution in alcohol a rotation of 178°↖, and for cinchonine of ↗244° the mean being ↗33°. My experiments gave for oxalate of cinchonicine a rotation of ↗18°, which is equal to 24·3° for the anhydrous alkaloid contained in the salt.

Although it would doubtless be more satisfactory to find an exact accordance in the number, I do not think that the difference is sufficient to make us pass over the approximation without careful notice.

By the action of nascent hydrogen upon the cinchona alkaloïds in acid solutions, a curious reaction takes place, which has been described by Schützenberger (*Ann. Chem. Pharm.*, cviii, 347).

The alkaloïds lose their power of forming crystalline salts, and form amorphous substances, which Schützenberger considers to differ

from the original alkaloids by containing one atom of water in excess. I am much inclined to doubt if the change is so simple. If a great surface of thin zinc-foil is placed in a strong solution of cinchonine or cinchonidine in sulphuric acid, and dilute sulphuric acid gradually poured in, there is no evolution of hydrogen till a very great excess of acid has been added.

When quinine or quinidine is thus treated, the reaction does not take place so regularly, and small quantities of hydrogen appear before the reaction is complete. Sodium amalgam may be substituted for zinc in this process, but the action is much less manageable, and though the resulting alkaloids are the same, they are apt to be discoloured in the process of formation.

The optical properties of these bodies are very similar to those of quinicine and cinchonicine. If during the progress of the reaction a portion of the alkaloid be separated from the zinc sulphate by ether and excess of ammonia, the rotatory power will be found to diminish as the reaction progresses, and when quinine or cinchonidine is experimented on, to become slightly right-handed; when the reaction is finished, the resulting alkaloid from quinine or quinidine is found to have a specific rotatory power of $\nearrow 55^\circ$ to the right in alcoholic solution, and that from either cinchonidine or cinchonine of $\nearrow 66^\circ$ also to the right. A further addition of sulphuric acid gives rise to a free evolution of hydrogen, but does not alter the rotatory power; a yellow colour is also developed, which renders the determination of the rotation of light in the polarimeter a matter of great difficulty. This is especially the case with quinine and quinidine; the yellow colour appears sooner, and is more intense than with cinchonine or cinchonidine, and if the acid is added too rapidly, or in too large quantities, the colour becomes too dark for observations.

By the action of ethyl iodide in the cold on an ethereal solution of these bodies, an ethyl base is formed, insoluble in ether, but of a dark colour, and defying purification even more effectually than the original alkaloid; it is obviously too impure for analysis, but a determination of the iodine in it was made, which gave 24.22 per cent. Its probable composition is therefore analogous to the ethyl bases of the original cinchona alkaloids; it was also found to deviate the polarised ray slightly to the right, but the colour was far too dark for accurate determinations.

The ethyl bases produced by the action of ethyl iodide or bromide on the cinchona alkaloids afford an opportunity of studying a very different mode of modification from those hitherto treated of. In them the isomerism still remains; each alkaloid yields its own ethyl base, distinguishable in its salts by solubility, hydration, or mode of crystallisation, as well as by its action on polarised light. These bodies have

already been described by Strecker (*Ann. Chem. Pharm.*, xci, 155), and by Dr. Stenhouse (*ibid.*, cxxix, 20), who have described the mode of preparation.

The iodide or bromide of ethyl-quinine forms readily in the cold, when an ethereal solution of the alkaloïd is mixed with ethyl iodide or bromide, and allowed to stand. The salt crystallises out, and may be purified by recrystallisation, the iodide from water, the bromide from a mixture of alcohol and ether.

The salts of the quinidine base are readily formed by heating the constituents in alcoholic solution for a short time. The iodide is almost insoluble in cold water, but slightly more so in hot water, from which it crystallises on cooling in fine needles; the bromide I have not been able to crystallise.

The combination takes place more slowly when cinchonidine or cinchonine is used, and it is necessary to continue the heat for some time; the iodides are somewhat more soluble than the iodide of ethylquinidine, which they resemble in appearance. The bromides are more freely soluble in both hot and cold water; they form in large, well-formed crystals.

It is important to avoid any needless exposure to heat of the alkaloïds in presence of an excess of ethyl iodide or ethyl bromide. By continuing the action for some time in sealed tubes at 100°, I have found, what appears to have escaped the notice of previous observers, that another molecule of the ethyl iodide or bromide enters into combination; this takes place most readily when ethyl-bromide is used. My experiments on the resulting bodies are still incomplete, but seem to show that they are the diiodethylates and dibromethylates of the alkaloids. If this proves correct, it would appear that the alkaloids act both as amines and as diamines, an analogous case being afforded by trimethyl-rosaniline, where one, two, or three atoms of methyl bromide can be combined with the base, the maximum number being in each case the number of atoms of nitrogen in the alkaloid. I hope shortly to present further results on these points to the Society.

It is possible that the composition of these bodies may throw some light also upon the remarkable facility with which the cinchona alkaloïds form acid as well as neutral salts with monobasic acids, while with the dibasic acids, sulphuric and tartaric, they form also, according to Dr. Hesse, salts containing two molecules of acid to one of the alkaloïd.

The specific rotatory powers of these bodies were found to be as follow:—The determinations are added of the iodine, bromine, and hydration, which were made to test the purity of the salts used.

Ethylquinine iodide, $C_{20}H_{24}N_2O_2,C_2H_5I + H_2O$: no water of crystallisation is lost over sulphuric acid, but all at 105°.

Iodine: theory 25·50; expt. 25·32
Hydration „ 3·62; „ 3·81 3·51

The deviation caused by a solution in alcohol containing ·05 grm. per c.c., showed that the specific rotatory power is 105° to the left.

Ethylquinine bromide, $C_{20}H_{24}N_2O_2,C_2H_5Br + 2H_2O$: the water of hydration is lost over sulphuric acid *in vacuo*.

Bromine: theory 17·00; expt. 16·68
Hydration „ 7·66; „ 7·61

The observed angle of rotation in an aqueous solution containing ·04 per c.c., and in an alcoholic solution of ·02 in a c.c., showed in each case a rotatory power of $117^{\circ}\nwarrow$.

Ethylquinine chloride, $C_{20}H_{24}N_2O_2,C_2H_5Cl + 3H_2O$,

Hydration: theory 12·21; expt. 11·95.

An aqueous solution of ·04 per c.c. showed the rotatory power to be $122\nwarrow$; but the presence of eight equivalents of hydrochloric acid raised this to 149°.

Ethylquinidine iodide appears from the iodine determinations to contain one atom of water, but only one-third of the requisite quantity is lost at 105°, and even at 120° the substance discolours before the whole is given off. The iodine was determined in different specimens, crystallised from water, and in one crystallised from alcohol, with the following results:—

Iodine: theory 25·50; expt. 25·69 25·61
25·74
Hydration „ 3·62; at 120° 2·03 2·00

The rotatory power proved to be, in alcoholic solutions containing ·015 grm. per c.c., $\nearrow 167^{\circ}$.

Ethylquinidine chloride, $C_{20}H_{24}N_2O_2,C_2H_5Cl + H_2O$,

Hydration: theory 4·43; expt. 4·60.

In an aqueous solution of 0·2 per c.c., the rotation of the polarised ray showed a specific power of $\nearrow 202^{\circ}$; eight equivalents of acid increased this to $\nearrow 257^{\circ}$.

Ethylcinchonidine iodide, anhydrous, $C_{20}H_{24}N_2O,C_2H_5I$,

Iodine: theory 27·37; expt. 27·52.

An alcoholic solution, containing ·02 per c.c., gave a specific rotation of $83^{\circ}\nwarrow$.

Ethylcinchonidine bromide, $C_{20}H_{24}N_2O : C_2H_5Br + H_2O$,
The water of crystallisation is driven off at 105°.

Bromine: theory 18·47; expt. 18·71
Hydration „ 3·87; „ 3·88

An alcoholic solution of ·04 per c.c. gave a specific rotatory power of 96°↖, an excess of acid increased this to 97°↖.

An aqueous solution of ·01 showed 97°↖; this was increased by excess of acid to 107°↖.

Ethyl cinchonidine chloride, $C_{20}H_{24}N_2O,C_2H_5Cl + 3H_2O$,

Hydration: theory 12·68; expt. 13·93.

In aqueous solution of ·016 per c.c., the specific rotatory power was found to be 97°↖; a great excess (10 equivalents) of acid raised this to 115°↖.

Ethylcinchonine iodide is anhydrous.

Iodine: theory 27·37; expt. 27·46.

An alcoholic solution of ·02 per c.c. gave ↗154° for the rotatory power.

Ethyl-cinchonine bromide; anhydrous.

Bromine: theory 19·28; expt. 19·33.

The specific rotatory powers observed in various solutions were as follows:—In an alcoholic solution of ·04 per c.c. ↗167°; in the same with excess of acid, ↗164°; in aqueous solution containing ·01, ↗162°; and with excess of acid, ↗167°.

Ethyl-cinchonine chloride, $C_{20}H_{24}N_2O : C_2H_5Cl + H_2O$,

Hydration: theory 4·6; found, 4·61.

The rotatory power in aqueous sol. of ·05 per c.c. is ↗169°, and with 10 equivalents HCl is ↗188°.

These numbers, if compared with those of the original alkaloïds, will be found very nearly proportional. Those of these salts of ethylquinine, ethylquinidine and ethylcinchonine approximate to the numbers which would be obtained by calculating the rotation for the proportionate quantities of the original alkaloïds in alcohol. The salts of ethylcinchonidine however do not follow the same rule, but agree very nearly with the rotatory power that I have found cinchonidine to possess in solution as bromide in alcohol, viz., 125°↖. The cinchonidine which was used in their preparation was tested by the polarimeter and found to give the right rotation.

By decomposing known weights of these salts with oxide of silver, we can obtain solutions of the hydrates of these bases of known strength for observation. The results are as follows:

Ethylquinine hydrate in aqueous solution containing ·0315 per c.c., shows a specific power of 23°↖.

Ethylquinidine hydrate in aqueous solution containing 0·371 per c.c., shows a specific power of ↗99°.

Ethylcinchonidine hydrate in aqueous solution containing ·0423 per c.c. shows a specific power of 75↖.

Ethylcinchonine hydrate in aqueous solution of ·0406 per c.c. shows a specific power of ↗148°.

These numbers are remarkable on account of the very small rotatory power they show; but that it is not owing to decomposition may be proved by neutralization with an acid, and the addition of potassium iodide: the iodides are thus recovered, with rotatory power and other properties unchanged; or else by exact neutralization with sulphuric acid, by which solutions are obtained giving optical results similar to those of sulphates obtained in other ways.

It is noteworthy that if we calculate the rotatory power of the alkaloïds contained in these solutions of their ethyl bases, we shall find the mean of the results in each pair very nearly the rotatory power of quinicine, the figures being for the mean of the quinine in ethylquinine and the quinidine in ethylquinidine ↗44°, and for the mean of cinchonidine in ethylcinchonidine and cinchonine in ethylcinchonine ↗43°. We have thus another example in which, though the specific rotatory power of the combination is widely different from that of the alkaloid contained in it when uncombined, the results obtained group themselves symmetrically round the points which we have found occupied by quinicine. These last-mentioned bases also combine with ethyl iodide, but are absolutely uncrystallisable when so combined, and of a dark colour, from which we cannot free them; this is much to be regretted, as it would be interesting to observe the relation of their rotatory powers to those we have been treating of.

The sulphates of these ethyl bases are so soluble that it is very difficult to obtain them by crystallisation; they were therefore prepared by the decomposition of weighed quantities of the iodides or bromides by silver sulphate, or by neutralising the solutions of hydrates obtained as already described.

The solutions thus obtained gave the following rotatory power: anhydrous ethylquinine sulphate in neutral aqueous solution, 134°↖; with ten equivalents of acid, 197°↖.

Anhydrous ethylquinidine sulphate in neutral aqueous solution, ↗194°; with ten equivalents of acid, ↗250°.

Anhydrous ethylcinchonidine sulphate in neutral aqueous solution, 101°↖; with ten equivalents of acid, 132°↖.

Anhydrous ethylcinchonine sulphate in neutral aqueous solution, ↗139°; with ten equivalents of acid, ↗161°.

We see thus that the sulphates of these bases differ from those of the original alkaloïds in possessing a proportionately lower rotatory power when compared with the chlorides, iodides, or bromides, but resemble them in the very great increase of the power caused by excess of acid. We find, therefore, to sum up the results of the previous pages, that the salts of the ethyl-bases, in which the distinctive characteristics of the alkaloid are not lost, give a series of numbers closely resembling those representing the rotatory powers of the salts of the original alkaloïds, but with somewhat lower values for the powers of the contained alkaloïds. In the two other cases treated of, on the other hand, where the distinctive characteristics of the isomeric alkaloïds are in other respects lost, the distinctive rotatory powers are lost also, and a new power obtained occupying a position between the former ones.

I may mention here that when I speak of alcoholic solutions, I mean solutions in alcohol of 90 per cent. Dr. Oudeman's' researches show that it is most important in all comparative trials to use solutions in all respects similar; doubtless much of the difficulty that we find in reconciling the results obtained by different observers arises from the different conditions under which they worked, which often are not clearly stated.

I have also, it will be seen, given whole numbers for the angles of rotation, as I do not wish to seem to pretend to greater accuracy than I have attained; the slight solubility of many of these substances prevents the use of solutions strong enough to give large angles; and it is most difficult, if not impossible, to obtain readings of the polarimeter identical to one minute. It is evident that a far greater accuracy than that would be required to give value to the decimal points of an angle over 100° if calculated from an observed angle under 10°.

The figures given are in all cases the average of several observations, and usually of two or more solutions. The angles of rotation are all of the yellow sodium ray.

ABSTRACTS OF CHEMICAL PAPERS PUBLISHED IN BRITISH AND FOREIGN JOURNALS.

General and Physical Chemistry.

On the Phenomena produced by Molecular Attraction in Capillary Spaces. By M. BECQUEREL (Compt. rend., lxxvi, 1037—1041).

ON placing a cracked tube filled with lead nitrate in a solution of potassium sulphate no precipitate can be observed either within or outside the crack. As, however, an electric current is found to circulate in a wire connecting two platinum plates immersed in the two liquids, we have a certain proof that one or both of the liquids have entered the crack. Other liquids give similar results. This remarkable fact, that no precipitate is formed between two liquids capable of double decomposition and in immediate contact with each other, is explained by the supposition that the attraction of the sides of the capillary space for both liquids is so strong as to overcome completely their mutual chemical attraction. When, on the other hand, nitric acid and mercury are separated in the same way, the mercury is strongly attacked, because the nitric acid, which alone traverses the crack, meets the metal, not inside but outside of the capillary space, so that the capillary forces do not interfere with the chemical reaction. In cases where the capillary attraction is very feeble for *one* of the liquids, this liquid only traverses the crack, but so slowly that the solid product of the double decomposition formed outside the crack is separated in the crystalline state. It appears to be a general fact that the decompositions do not take place unless the diameter of the crack exceeds some $\frac{1}{1000}$ of a millimeter, the limits being somewhat different for different liquids.

The following conclusions, given at the end of the paper (which itself is only an abstract), seem to refer to experiments described in the original communication only:—

1. The liquid film adhering to the sides of the capillary space is not only capable of conducting electricity in the manner of solid bodies, but it possesses other properties which have to be taken into account in the study of electro-chemical phenomena.

2. On operating with certain saturated non-metallic solutions capable of decomposing each other with formation of a solid precipitate, this precipitate is found not to be formed inside the capillary space when the sides of the latter consist of glass. This result is ascribed to the prevalence of the capillary over the chemical forces.

3. Solid particles in a state of great subdivision and constantly kept moist behave like solid conductors in their contact with an

oxidisable metal, a multitude of electro-capillary currents being formed which act like ordinary galvanic currents.

4. Simple electro-capillary couples may, on account of their feeble intensity, be used as units in order to compare electro-motive forces; however, as they are not constant, only the first impulses can be employed for measuring purposes.

5. When the solid precipitate is formed inside the cracked tube, it is a proof that the capillary affinity of the substance of the tube is smaller for the external than for the internal liquid, and *vice versâ.*

R. S.

Lecture Experiments on Combustion. By KARL HEUMAN (Deut. Chem. Ges. Ber., vi, 231—233).

BY introducing a current of air or oxygen into the inner part of a flame and lighting it there, the author furnishes a neat and convincing proof of the presence of unburnt gas in this part of the flame. The apparatus employed consists of a glass cylinder 30 cm. long and 6 cm. wide, in the lower end of which are inserted two glass tubes. One of them, 40 cm. long and 1·2 c.m. wide, passing vertically through the centre, projects a little over a piece of wire-gauze placed over the top of the cylinder. The other glass tube supplies the interior of the cylinder with gas; when this is lighted, a current of air is driven through the central tube and lighted by raising the latter to the mantle of the flame. On lowering the tube again and depressing the flame with a piece of wire gauze, the central oxygen-flame is spread out in the shape of a tulip, and surrounded by a sharply defined luminous cone. A beautiful crimson colour may be imparted to the inner flame by passing the air-current through a piece of caoutchouc-tubing containing a little powdered strontium nitrate. The use of a double-acting bellows is recommended to obtain a sufficiently continuous air-current.

R. S.

Researches on some Oxidising and Reducing Agents. By JULIUS THOMSEN (Deut. Chem. Ges. Ber., vi, 233—239).

THE heat-moduli of the characteristic reactions of the following reducing agents: sulphurous acid, ferrous sulphate, ferrous chloride, stannous chloride, and of the oxidising agents: chlorine, bromine, hypochlorous acid, potassium permanganate, manganese peroxide, chromic acid and hydric peroxide have been determined by the author in his research on the affinity of oxygen for the metalloids. The present paper gives only the numerical results and rules for their application, without entering into the methods by which they have been obtained.

TABLE I.

Reaction.	Q.	
(SO_2Aq,Cl_2)	73907	Heat-units for 1 mol. of chlorine.
$(2FeCl_2Aq,Cl_2)$	54810	
$(2FeSO_4Aq,Cl_2)$..........	47039	
$(SnCl_2Aq,Cl_2)$............	73875	
(SO_2Aq,O)	63634	Heat-units for 1 atom of oxygen.
$(2FeClAq,O,H_2Cl_2Aq)$	44537	
$(2FeSO_4Aq,O,SO_3Aq)$	30800	
$(SnCl_2Aq,O,H_2Cl_2Aq)$	63602	

The author gives the following rule for using the above results for purposes of calculation:—If one of the reducing agents of Table I is used in order to remove the oxygen or chlorine from a body, and if the heat evolved in this process is = R for every molecule of chlorine or every atom of oxygen removed, then the quantity of heat consumed in the decomposition of the compound which furnished the oxygen or chlorine is represented by Q − R. The author remarks that the above numbers do not express the relative strength of the several reducing agents.

TABLE II.

Reaction.	Q for 1 atom of oxygen.
(Cl_2,H_2,Aq)—(H_2O)..........	10273
(Cl_2Aq,H_2)—(H_2,O)..........	5403
(Br_2,H_2,Aq)—(H_2,O)	− 11605
(Br_2Aq,H_2)—(H_2,O)..........	− 12683
(Cl,H,Aq)—(Cl,O,H,Aq)......	10993
$(Mn_2O_8K_2Aq,6HClAq)$	13117
$(Mn_2O_8K_2Aq,3SO_3Aq)$	15287
$(Mn_2O_8K_2Aq,2HClAq)$	19865
$(Mn_2O_8K_2Aq,SO_3Aq)$	21128
$(\overline{\overline{Mn}}O,SO_3Aq)$	6526
$(2CrO_3Aq,3SO_3Aq)$	12295
—$(2\overline{\overline{Mn}}O,O_3,2\overline{K}Aq)$	10698
—$2(\overline{\overline{Mn}},O_5,2\overline{K}Aq$	− 1563
—$(\overline{\overline{Mn}}O)$	− 19954
—$(2\overline{\overline{Cr}},O_3,Aq)$	− 4145
—(H_2O,O,Aq)	+ 23318

Rule.—If a substance is oxidised by one of the reagents here indicated, the quantity of heat developed by each atom of oxygen absorbed is greater by the value of Q, given in the above table for the reagent in question, than what would have been developed if the same oxidation had been effected by free oxygen.

Attention is drawn to the great difference in the quantity of heat produced by the different oxidising agents, and it is pointed out that those which produce the most heat are by no means always the best. How carefully the secondary reactions have to be considered can be seen from the following instance. When chlorine acts upon sodium

sulphite, the heat produced is not due simply to the formation of sulphuric and hydrochloric acids, but partly also to the reaction of the hydrochloric acid formed upon the other product, sodium sulphate.

R. S.

On the Affinity of Oxygen for Chlorine, Bromine, and Iodine.

By JULIUS THOMSEN (Deut. Chem. Ges. Ber., vi, 429—435).

Chloric Acid.—The heat of formation of this acid has been determined by two methods. On decomposing potassium chlorate in the dry way, it was found that—

$$-(ClK,O_3) = 9713 \text{ heat-units.}$$

Substituting this value in the difference of the following two equations:—

$$(K_2,Cl_2,O_6) + 2(K,ClO_3,Aq) = (K_2,O,Aq) + (Cl_2,O_5,Aq) + (2\overline{K}Aq,Cl_2O_5Aq),$$

$$(K_2,Cl_2) + 2(KCl,Aq) = (K_2,O,Aq) + 2(Cl,H,Aq) + 2(\overline{K}Aq,ClHAq) - (H_2,O).$$

and making use of the relation—

$$(K_2,Cl_2,O_6) - (K_2,Cl_2) = 2(ClK,O_3) = -19426 \text{ heat-units,}$$

we obtain—

$$(Cl_2,O_5,Aq) = -20381 \text{ heat-units,}$$

and because

$$2(Cl,O_3,H,Aq) = (Cl_2,O_5,Aq) + (H_2,O),$$

it follows that

$$(Cl,O_3,H,Aq) = 23988 \text{ heat-units.}$$

The heat evolved by every molecule of chloric hydrate when it is reduced in aqueous solution by sulphurous acid, is—

$$R = (ClO_3HAq,3SO_2Aq) = 3(SO_2Aq,O) + (Cl,H,Aq) - (Cl,O_3,H,Aq) = 206324 \text{ heat-units,}$$

from which we obtain—

$$(Cl,O_3,H,Aq) = 23893 \text{ heat-units.}$$

As this result agrees very well with that obtained by the decomposition of potassium chlorate in the dry way, the author thinks himself justified in rejecting Favre's number—

$$(Cl_2,O_5,Aq) = \begin{cases} -130470 & \text{Favre.} \\ -\ \ 20477 & \text{Thomsen.} \end{cases}$$

The other heat reactions of chloric acid are—

$$\begin{aligned} (Cl,O_3,H,Aq) &= 23940 \text{ heat-units.} \\ (ClHAq,O_3) &= -15375 \quad " \\ (Cl_2,O_5,Aq) &= -20477 \quad " \end{aligned}$$

$$(2\bar{K}Aq,Cl_2O_5Aq) = 27520 \text{ heat-units.}$$
$$(KClO_3,Aq) = -10044 \quad ,,$$
$$(ClK,O_3) = -\ 9761 \quad ,,$$
$$(ClKAq,O_3) = -15365 \quad ,,$$

Bromic Acid.—On reducing an aqueous solution of bromic acid by means of stannous chloride, the author found—

$$R = (BrO_3HAq,3SnCl_2H_2Cl_2Aq) = 3(SnCl_2Aq,O,H_2Cl_2Aq) + (Br,H,Aq) - (Br,O_3,H,Aq) = 213792 \text{ heat-units.}$$

from which follows—

$$(Br,O_3,H,Aq) = 5384 \text{ heat-units,}$$

and—

$$(BrHAq,O_3) = -22992 \text{ heat-units.}$$
$$(Br_2,O_5,Aq) = -57589 \quad ,,$$

Hence the affinity between the constituents of bromic acid is considerably less than between those of chloric acid. This result, whilst contrary to the opinion that the greater affinity for hydrogen corresponds to a smaller one for oxygen is quite in accordance with the fact that bromic acid is more easily decomposed than chloric acid.

Iodic acid, on being reduced by stannous chloride, gave—

$$R = (IO_3HAq,3SnCl_2H_2Cl_2Aq) = 160440 \text{ heat-units.}$$

From this and the following direct determinations—

$$(IO_3H,Aq) = -\ 2166 \text{ heat-units.}$$
$$(\bar{K}Aq,IO_3HAq) = 13808 \quad ,,$$
$$(\bar{K}Aq,IO_3KAq) = 608 \quad ,,$$
$$(IO_3HAq,IO_3KAq) = 192 \quad ,,$$

we obtain the other heat reactions of iodic acid—

$$(I,H,Aq) = 13171 \text{ heat-units.}$$
$$(I,O_3,H) = 45703 \quad ,,$$
$$(I,O_3,H,Aq) = 43537 \quad ,,$$
$$(IHAq,O_3) = 18717 \quad ,,$$

Thomsen's results differ considerably from Ditte's—

$$(I_2,O_5,Aq) = \begin{cases} 26018 \text{ heat-units} & \text{Ditte.} \\ 18717 \quad ,, & \text{Thomsen.} \end{cases}$$

Periodic acid reduced by stannous chloride gave—

$$R = (IO_4HAq,4SnCl_2,H_2Cl_2Aq) = 227480 \text{ heat-units.}$$

The latent heat of solution of the hydrate of iodic acid was—

$$(IO_6H_5,Aq) = -1379 \text{ heat-units.}$$

From these reactions the others can be calculated—

(I,O_4,H,Aq)	=	40100	heat-units.
$(I,O_4,H,2H_2O)$	=	41480	„
$(IHAq,O_4)$	=	26930	„
(I_2,O_7,Aq)	=	11843	„
(IO_6H_5,Aq)	=	− 1380	„
$(\overline{K}Aq,H_5O_6IAq)$	=	5150	„
$(2\overline{K}Aq,H_5O_6IAq)$	=	26590	„

The affinity between the constituents of periodic acid is somewhat smaller than that of iodic acid, but it is positive in both acids.

Hypochlorous Acid.—The reactions given in the author's paper on oxidising and reducing agents are—

(Cl,O,H,Aq)	=	28322	heat-units.
(Cl,HAq,O)	=	−10993	„
(Cl_2,O,Aq)	=	−11713	„
$(\overline{K}AqClOHAq)$	=	9685	„

Favre's result—

$$(Cl_2,O,Aq) = -15000 \text{ heat-units},$$

found by decomposing hypochlorous acid with hydrochloric acid is rejected by Thomsen, who noticed that the above reaction varies with the concentration of the acid.

Comparing the values of the total heat of formation of chloric, bromic and iodic acids—

	Cl. Heat-units.	Br. Heat-units.	I. Heat-units.
(R,O_3,H,Aq)....	23940	5384	43537
(R_2,O_5,Aq)......	−20477	−57589	+18717

.... considering that

$$\tfrac{1}{2}(43537 + 5384) = 24460.$$
$$\tfrac{1}{2}(18717 - 57589) = -19936,$$

we see that *with regard to the affinity for oxygen, chlorine stands nearly midway between bromine and iodine.* The author is inclined to think that bromine and chlorine, although in many respects allied with iodine, ought to be considered as a special group from which iodine must be excluded.

R. S.

Thermochemical Determinations of the Affinities of Oxygen for Sulphur, Selenium, and Tellurium. By JULIUS THOMSEN (Deut. Chem. Ges. Ber., vi, 522—532).

To his former determinations of the heat-moduli of the reactions—

$(S,O_2.Aq)$	=	78770	heat-units,
(S,O_3,Aq)	=	142404	„
(SO_2Aq,O)	=	63634	„

the author has now added the following for selenium—

$$
\begin{aligned}
(SeO_2,Aq) &= -918 \text{ heat-units,} \\
(Se,O_2) &= 57710 \quad ,, \\
(Se,O_2,Aq) &= 56792 \quad ,, \\
(Se,O_3,Aq) &= 75682 \quad ,, \\
(SeO_2Aq,O) &= 18890 \quad ,, \\
(SeO_2,O,Aq) &= 17972 \quad ,,
\end{aligned}
$$

and for tellurium—

$$
\begin{aligned}
(Te,O_3,Aq) &= 100900 \text{ heat-units.} \\
(Te,O_2,H_2O) &= 76300 \quad ,, \\
(TeO_2Aq,O) &= 24600 \quad ,,
\end{aligned}
$$

Selenium.—The affinity between oxygen and selenium in selenious acid was determined by reducing an aqueous solution of this acid with a solution of monosodic sulphide. The chemical and the heat reactions in this process may be expressed by the equations—

$$SeO_2Aq + HClAq + 2NaSHAq = 2NaClAq + 2H_2O + 2S + Se,$$

and—

$$R \text{ (heat evolved)} = 2(\bar{N}aAq,HClAq) - 2(\bar{N}aAq,SH_2) + 2(H_2,O) - 2(S,H_2) - (Se,O_2,Aq) = 73398 \text{ heat-units,}$$

from which, using the results of the preceding abstract, we obtain

$$(Se,O_2,Aq) = 56792 \text{ heat-units,}$$

and as the heat produced by the solution of selenious acid in water was found to be

$$(SeO_2,Aq) = -918 \text{ heat-units,}$$

it follows that

$$(Se,O_2) = 57710 \text{ heat-units.}$$

The affinity between oxygen and selenium in selenic acid was determined by oxidising an aqueous solution of selenious acid with hypochlorous acid. The reaction is

$$SeO_2Aq + ClOHAq = SeO_3Aq + HClAq,$$

and R, or the heat evolved, was found to be = 29883 heat-units. By subtracting the *oxidation constant* of hypochlorous acid (given in the preceding abstract) from R, we obtain

$$(SeO_2Aq,O) = 18890 \text{ heat-units,}$$

and adding to this $(Se,O_2,Aq) = 56792$ heat-units, we have

$$(Se,O_3,Aq) = 75682 \text{ heat-units.}$$

Tellurium.—The author had to operate with smaller quantities of substance than with other elements. The affinities in tellurous acid were determined by reducing a solution of tellurous acid in hydrochloric acid by means of stannous chloride—

$$R = (TeO_2,HClAq,2SnCl_2Aq) = 2(SnCl_2Aq,O,H_2Cl_2Aq - (Te,O_2,H_2O) = 50300 \text{ heat-units.}$$

This, with the results given in the previous abstract, gives

$$(Te,O_2,H_2O) = 76300 \text{ heat-units.}$$

The heat-modulus for every atom of oxygen taken up by tellurous acid when it is oxidised in a nitric acid solution, by potassium permanganate, amounts to 44440 heat-units. By subtracting from this

$$(Mn_2O_8K_2Aq,2HClAq) = 19865 \text{ heat-units,}$$

we obtain $(TeO_2Aq,O) = 24600$ heat-units, and from this, by the addition of (Te,O_2,H_2O),

$$(Te,O_3,Aq) = 100900 \text{ heat-units.}$$

Comparing the results for the three elements of this group, *we find the numbers for selenium smaller than those for sulphur or tellurium;* this is important, as not being in accordance with a fact which chemists had of late been inclined to consider as nearly general, namely, that the elements in the different groups, when arranged according to increasing atomic weights and to increasing affinities, follow each other either in the same or in the inverse order. This exception is not an isolated fact, as the author has proved (see above, p. 1190) that the affinity of oxygen for chlorine and iodine is greater than that for bromine; whilst concerning their affinities for hydrogen, bromine stands indeed midway between the two others, as might be expected, from its atomic weight being intermediate between those of the others.

R. S.

On the Common Constant of Affinity. By JULIUS THOMSEN (Deut. Chem. Ges. Ber., vi, 239—242).

IT is shown that in several series of analogous chemical reactions the heat-moduli can be expressed as multiples of numbers which lie very near 18427. This number is called the common constant of affinity.—(Comp. *Chem. Soc. J.* [2], x, 457.) R. S.

On the Reciprocal Displacements of the Hydracids. By M. BERTHELOT (Compt. rend., lxxvii, 308—316).

IT is well known that the reciprocal displacements of the hydracids are very often the reverse of those exhibited by the corresponding metalloids. Thus on the one hand chlorine displaces bromine, and both expel iodine from its compounds with silver and the alkali-metals, while on the other hand hydriodic acid decomposes bromides and chlorides. The author has already explained these facts by showing (*Compt. rend.*, lxiv, 414) that the reaction which occurred by preference was always the one which evolved most heat. But the calculations having been founded on determinations which more recent experience has rendered doubtful, he has reinvestigated the thermic relations of the halogens and their hydrogen-acids with the metals potassium, silver, and mercury. The result confirms in every way his previous views, with the exception that the heat developed by the reaction of potassic hydrate with the three hydracids is practically the same for

each, when the salts produced are obtained *in solution.* But even in this case the heat of formation of the *solid* salts is in accordance with the general law.

It is found that no constant difference exists between the thermic effects either of the halogens or of the hydracids. Thus, whilst with potassic hydrate the three acids evolve identical quantities of heat, the formation of mercuric iodide from the base and acid disengages 19·2 heat-units more than the formation of the chloride; with silver oxide and hydriodic acid the heat exceeds by 11·2 units that of the corresponding reaction with hydrochloric acid. Similarly the substitution of chlorine for iodine in the mercury salt disengages less heat than in the salt of any other metal. In the case of the alkali-metals, however, and also with certain non-metallic chlorides, &c., an approximation to a constant difference is observed. It is incidentally mentioned that the solution of mercuric iodide in potassic iodide evolves considerable heat.

Although the heat of formation of the three potassium salts is the same, it is undeniable that the acid with a higher equivalent will replace one with a lower. This fact has been carefully studied by mixing each of the three hydracids with the potassium salt of the two others in dilute solution, and then evaporating the mixture. The following facts were then observed:—An excess of hydriodic acid (2 equivalents) displaces almost completely the two other acids, and a similar excess of hydrobromic acid as perfectly expels hydrochloric acid; but with single equivalents of the acid and salt the substitution is incomplete, the residue always containing salts of both acids, that with the higher equivalent, however, preponderating. The numbers furnished by reciprocal reactions are generally nearly the same; and further, although hydrochloric acid is able to expel a small proportion of the other acids, yet even when in large excess it does so very imperfectly.

These facts admit of the following explanation:—The two hydracids divide the base between them when the solution is dilute, but when during evaporation the point is reached at which a definite hydrate (or rather a system in which the hydrate, the anhydrous acid, and the vapour of water are in a state of equilibrium) begins to pass off, the hydrochloric acid escapes with greatest facility, because in such a system this acid possesses a higher tension of dissociation than the two others at the same temperature (*Compt. rend.*, lxxvi, 742); and though the stability of the hydrates of the two latter is very nearly the same, yet the greater volatility of the bromhydric hydrate is the cause of its passing off in preference to the less volatile iodhydric hydrate. Nevertheless, since the anhydrous acid in both the latter hydrates possesses a certain tension of dissociation, it follows that when the two acids are present in equivalent proportions, or when the more volatile preponderates, a portion of the less volatile will in all cases be lost.

That a division of the base between the two acids actually takes place may also be demonstrated by adding concentrated hydrochloric acid to a saturated solution of potassic iodide, when a precipitate is obtained consisting of almost pure potassic chloride.

M. J. S.

New Process for the Condensation of Vapours held in Suspension by Gases. By E. PELOUZE and P. AUDOUIN (Compt. rend., lxxvii, 264—268).

IT is well known how difficult it is to separate by simple cooling the vapours of volatile substances held in suspension by a large volume of permanent gas. The authors, who consider these vapours to exist, when the temperature is below their boiling point, in a fine pulverulent form, propose to effect their condensation by forcing the gas through a series of small apertures and causing the streams to impinge on a flat surface placed opposite. They consider that by this means the particles of the condensable substance are brought into contact with one another, and that the larger globules thus formed adhere to the surface against which they are driven, and are thus removed from the gas.

The method has been applied both on the small and large scale to the separation of tar, ammonia, carbon sulphide, &c., from coal gas, and the result is described as highly satisfactory. One great advantage is the small size of the apparatus.

M. J. S.

On the Mechanical Separation of Complex Crystals. By K. HAUSHOFER (J. pr. Chem. [2], vii, 147—152).

IF complex crystals could be so finely powdered that the particles represented the different substances of which the crystals are composed, then by taking advantage of the differences in specific gravity, we ought to be able to separate the several constituents by washing.

Even if only a part of the crystal was sufficiently pulverised, the different sediments obtained in the process of washing ought to possess a different chemical composition.

The author experimented with ankerite, siderite, &c., and found in some cases that the various sediments did not differ in chemical composition, while in other cases there was a sufficient difference to show that separation had been effected to a slight extent. Hence he concludes that there are crystallised mixtures of isomorphous and heteromorphous bodies, and in cases where the bodies show in their composition simple stoïchiometrical relations, they must be regarded as definite chemical compounds.

G. T. A.

Calorimetric Pyrometer for the Determination of High Temperatures (Chemical News, xxviii, 116).

On some Forms of Laboratory Apparatus. By WOLCOTT GIBBS (Chemical News, xxviii, 30).

Inorganic Chemistry.

On the Behaviour of the Diamond and Graphite at High Temperatures. By G. Rose (Pogg. Ann., cxlviii, 497).

It is well known that the diamond, graphite, and charcoal are allotropic bodies; when burnt, they all form carbonic anhydride. Conflicting statements exist, however, concerning the relative behaviour of these different modifications of carbons when exposed to high temperatures in a vacuum; and it is with a desire to reconcile these that the author has been led to make the following experiments:—

In conjunction with Dr. W. Siemens, he attempted to ignite the diamond in a vacuum by means of a powerful electrodynamic apparatus. The diamond was placed between carbon poles and allowed to rest on one of them. It split into fragments as soon as a red heat had been reached. A second experiment was made with the same result. The diamond was partially changed to graphite on the surface, as the heat had probably been applied too suddenly. A third experiment was made, in which the diamond was placed in a hole bored in a small cube of the hard carbon which deposits in gas retorts, and this cube was placed in a graphite crucible filled with wood-charcoal, and heated for half an hour to the melting point of cast-iron. The diamond suffered no change. A second experiment was made with a rosette-cut diamond, but with this difference, that the heat was applied only for ten minutes. On examination, the surface was found to be opaque and black, with a bright metallic lustre. This crust was confined to the surface, for on breaking the diamond, the interior was unchanged. The heat had been applied for too short a time; circumstances prevented the author from repeating the experiment, and exposing the diamond to more continued ignition.

Schrötter, who made similar experiments, found that on one occasion the surface of the diamond had become dull; and a diamond wrapped in platinum foil was blackened, with black streaks running through the interior, while the foil was fused to a button.

The diamond, when heated in a muffle through which a current of air is passing, grows smaller and smaller, keeping its brilliancy till it finally disappears, and emitting a faint light at the last moment. The octohedral and cleavage surfaces become indented with microscopic triangular impressions, which resemble those formed when a crystal is attacked by an acid. The edges are in no case rounded off in burning; each atom goes at once from the solid into the gaseous state. The diamond shows no sign of changing to graphite during combustion, but sometimes becomes opaque. A small splinter may even be burnt before the blowpipe; it does not blacken. Fourcroy, in 1782, on exposing diamonds to a high temperature in a muffle, found that they became covered with a black coating. This the author explains by supposing that, as the older form of muffles had side openings, the smoke from the furnace might have coated the diamonds. However, all accounts of experiments in which diamonds have been exposed in

the focus of a concave mirror, describe them as becoming black; the same occurs in the oxyhydrogen flame. Guyton Morveau relates that a diamond exposed to concentrated rays of the sun, burns away, at the same time tumefying and turning black. Jaquelin heated a diamond in an atmosphere of carbonic anhydride with the oxyhydrogen blowpipe; where it was touched by the point of the flame, it became smooth and shining, but did not blacken at all. When placed between the poles of a Bunsen's battery of 100 elements it was transformed into graphite, which was still hard enough to scratch glass.

The small angular indentations on the diamond are regular, and lie on the octohedral surface in such a manner that their sides are parallel to the edges of the octohedron; they are probably produced by the surfaces of the icositetrahedron. A measurement confirmed this view. These indentations can easily be produced on splinters before the blowpipe; they are not to be confused with the indentations often found on octohedrons, which are produced solely by want of substance in the crystal.

Some diamonds are naturally black. This appears to be a pseudomorphose of graphite into diamond, but is possibly produced on the diamond by heat. A black diamond heated in melting saltpetre, underwent no change, showing that the blackness was due to graphite, not to amorphous charcoal.

A variety of diamond called "Carbonado," or "Carbonate," is found in the Soap Mountains of Bahia. Pieces of this substance are said to have been found from one to two pounds in weight. A specimen from the Berlin Museum has no surface, but appears porous when examined with a lens; its colour is reddish-grey, and four pieces of carbonado exhibited a specific gravity of 3·012, 3·341, 3·416, and 3·255 respectively, which is obviously that of the diamond. Carbonado heated to whiteness in a muffle gave off small bubbles, losing its sharply cut edges, and becoming more porous; its surface also grew dull. Göppert ascribes the formation of bubbles to the carbonic anhydride which escapes, but nothing similar to this occurs in the combustion of the diamond; it may be assumed, therefore, to be due to air escaping. Rivot found in three specimens of carbonado 2·03, 0·24 and 0·27 per cent. of ash, consisting probably of alumina coloured by iron. Carbonado may be used for polishing diamonds, and for boring machines. Only three specimens of carbonado are known which possess a crystalline form; whether they are true crystals or not is a matter of doubt.

An experiment was made to decide whether the diamond, laminated graphite from New York State, or compact graphite would burn most quickly. In thirteen minutes, while the compact graphite had completely disappeared, 27·45 per cent. of laminated graphite were consumed, and 97·76 per cent. of the diamond. The shape of the specimens was different, and this may have influenced the result. Probably the compact graphite was amorphous carbon, as it deflagrated when heated on charcoal. The specific gravity was also lower than that of the graphite.

W. R.

New Sulpho-salts. By R. Schneider (Pogg. Ann., cxlviii, 625—639).

In a former paper (this Journal [2], ix, 313) the author has described potassium-palladium sulphopalladate ($K_2S.Pd_2S\}PdS_2$). This salt when treated with hydrochloric acid gives up the whole of its potassium; neither hydrogen nor sulphuretted hydrogen is evolved, the residue does not contain free sulphur, and little or no sulphate is produced. This reaction the author believes to take place in two phases:—

1. Hydrogen is substituted for potassium, the resulting compound having the composition $H_2S.Pd_2S\}PdS_2$.
2. By the action of atmospheric oxygen, the compound $Pd_2S_2\}PdS_2$ is formed; thus, $H_2S.Pd_2S\}PdS_2 + O = H_2O + Pd_2S_2\}PdS_2$.

To the new salt the constitutional formula $\left.\begin{matrix}PdS\\PdS\end{matrix}\right\}PdS_2$ is given, and it is regarded as a loose combination of the monosulphide and disulphide of palladium, the disulphide in this compound exhibiting very nearly the same properties as when it exists in the free state. When it is strongly ignited, half of the sulphur of the disulphide is driven off in combination with oxygen; the residue consists of palladium monosulphide, which, as thus obtained, is a blackish-grey crystalline powder, very slightly acted on by aqua regia. At a bright red heat it loses part of its sulphur, palladium subsulphide, Pd_2S, being formed.

Silver-palladium Sulphopalladate.—When two molecules of silver nitrate in a dilute aqueous solution are added to one molecule of potassium-palladium sulphopalladate suspended in water, the latter salt loses its blue colour, becomes whitish grey, and at the same time an amount of potassium nitrate, equivalent to that of the silver nitrate used, is formed. A new salt is formed, which, however, contains varying amounts of finely divided metallic silver. By using a dilute ammoniacal solution of silver nitrate, and treating the product with cold nitric acid for a short time, a salt is produced having the formula $Ag_2S.Pd_2S\}PdS_2$. This substance forms whitish-grey metallic-looking hexagonal plates. It is characterised by its great stability, being unacted on by water, ammonia, potash, or even boiling hydrochloric acid. The residue after heating out of contact with air is partially decomposed by boiling nitric acid or aqua regia. Heated in the air it absorbs oxygen, the residue when heated with water yielding silver sulphate, but no palladium salt. On heating it in a stream of hydrogen sulphuretted hydrogen is evolved. Boiling nitric acid removes all the silver and a part of the palladium from the residue, a grey crystalline powder remaining, which is probably palladium subsulphide.

Tetra-platinous Sulphostannate.—By treating a very dilute solution of 1 molecule of platinum tetrachloride with 2 molecules of stannous chloride, and adding ammonia to the resulting dark brown liquid, a brownish-black precipitate is obtained having the composition $Pt_3Sn_6O_{10}$ (platinous stannous stannate). When four parts of this substance are fused with six parts of soda and about eight parts of sulphur, a black-grey crystalline powder is obtained, having the com-

position Pt_4SnS_6. This compound the author regards as analogous to sodio-platinous sulphostannate (*Watts's Dict.*, *Supp.*, 1077). Its constitutional formula therefore becomes $Pt''S.Pt''S.Pt''S.Pt''S.\}^{iv}SnS_2$. The crystalline black-grey powder, appears under the microscope to consist of a mass of small lustrous needles. It is unchanged in the air, but when heated it is completely decomposed, the residue consisting seemingly of metallic platinum mixed with platinous stannate. Boiling hydrochloric or nitric acid has no action upon this substance; boiling aqua regia decomposes it very slowly.

Tetra-platinous Sulphoplatinate.—It is generally stated that the product obtained by fusing equal parts of sulphur and ammonium chloroplatinate is platinous sulphide, PtS. The analyses, however, of this salt do not very closely agree with the numbers required by the above formula. They point to the formula Pt_5S_6, which is confirmed by the author's analyses. This salt is most easily prepared by fusing together for 8—10 minutes at a bright red heat 1 part ammonium chloroplatinate, $1\frac{1}{2}$ parts sulphur, and $1\frac{1}{2}$ parts soda. It forms steel-grey needles, having a metallic aspect and belonging to the rhombic system. It is unchanged in the air when dry, but if the moist substance be heated on the water-bath it absorbs oxygen, and then contains sulphuric acid. Heated in carbon dioxide it loses one-sixth of its sulphur, platinous sulphide remaining; heated in the air, the sulphur is entirely burned away. *Strongly* heated in a stream of hydrogen it is entirely reduced. It is unacted upon by boiling hydrochloric or nitric acid, but is slowly attacked by boiling aqua regia. Fused with nitre, it is easily and completely decomposed. The constitutional formula assigned to this salt is $Pt''S.Pt''S.Pt''S.Pt''S.\}^{iv}PtS_2$.

M. M. P. M.

Nitrates in Soils.

By Th. Schloesing (Compt. rend., lxxvii, 203—209, and 353—356).

The first part of this research relates (A.) to the influence of the proportion of oxygen in the atmosphere contained in the soil, combined (B.) with the influence of the state of hydration of the soil, in promoting nitrification and the combustion of the carbon of the organic matter.

Five portions of soil, each weighing two kilograms, were treated with mixtures of air and oxygen in various proportions. The mixtures, which were previously freed from carbon dioxide and ammonia, were supplied by the apparatus mentioned in this Journal [2], x, 788. The atmosphere in the soil was, therefore, kept constant in composition. The soil employed contained 15·9 per cent. of water and 0·263 per cent. of nitrogen. The percentage composition of its cinereal constituents was 14·6 of clay, 19·5 of fine limestone, 48 of siliceous sand, and 17·7 of calcareous sand. In the following table are given the percentages of oxygen in the atmospheres employed, and the quantities of carbon dioxide and nitric anhydride formed. Series A lasted from July to November. During July and August the carbon dioxide evolved was determined. The mean quantity per kilogram

in twenty-four hours, with the mean temperature, is given in the table. The *total* nitric anhydride per kilogram formed in the whole period is also given. In Series B, which lasted from November to July, the moisture in the soil was raised to 24 per cent. The amount of carbon dioxide evolved during November and December, and the total nitric anhydride formed in the whole period were determined. The results are given as in A.

Experiment	I.		II.		III.		IV.		V.	
Percentages of oxygen in atmosphere	1·5		6·0		11·0		16·0		21·0	
Series	A.	B.	A.	B.	A.	B.	A.	B.	A.	B.
Mean temperature first two months	24°·3	14°·3	24°·0	14°·5	23°·1	15°·0	21°·2	16°·1	25°·2	14°·2
Milligrams of carbon dioxide in 24 hours per kilo.	10·4	?	16·6	15·9	16·1	16·0	15·1	16·6	19·0	16·0
Milligrams of nitric anhydride per kilo.	45·7	?	95·7	199·0	132·5	222·0	[246·6]	203·0	[162·6]	225·0

In Series A it will be noticed, says the author, that when once the proportion of oxygen reaches 6 per cent. no further increase of oxygen produces an increase of carbon dioxide.* The amounts of carbon dioxide evolved in September and October (not given in the table), when the mean temperature was 16°, were only one-half of those evolved in July and August, showing how greatly increase of temperature favours the slow combustion of the carbon. In Series B it will be seen that the presence of water acts in the same direction, the amounts of carbon dioxide evolved being equal to those in A, although the mean temperature had fallen about 10°. In fact, the first experiment of Series B was made with pure nitrogen, and yet the soil contained enough oxygen in the organic matter and the reducible cinereal matter to furnish 9 mgms., or about 90 per cent. of that produced in A, with an atmosphere containing 1·5 per cent. of oxygen.

The nitric anhydride in Series A, unlike the carbon dioxide, increases with the increase of oxygen, though not in the same proportion. (The figures in brackets are supposed by the author to have been accidentally interchanged.) In Series B, which lasted nearly twice as long as A, the amount of nitric anhydride is in one case only double that in A; from that point the proportion in B to that in A continually decreases if the author's explanation of the figures in brackets is correct.† Here, again, as with the carbon dioxide, the first experiment was made with pure nitrogen, when the unexpected result was obtained of the total disappearance of the nitric anhydride (64 mgms. per kilo.) which the soil naturally contained. This was, doubtless, due to the reducing action of the organic matter.

The author arrives at the conclusion that the combustion of organic

* It will be remarked that this is not true if the above figures are correct, since Experiment V shows a directly proportionate increase compared with Experiment IV. It may be, however, that 19 is a misprint for 16.

† The employment of a different length of time in B to that in A renders the results not strictly comparable, since the mean temperature, amongst her conditions, of the period, July to November, must have differed from that of November to July.

matter and formation of nitrates may be very active, provided abundance of moisture be present, even when the atmosphere in the soil is very poor in oxygen.

The preceding observations show that when the atmosphere in the soil contains no oxygen, the nitric anhydride present is reduced, and the fact has been noticed by other investigators. In order to determine what are the products of the reduction the following experiments were made:—Twelve kilograms of the same soil that was employed in the previous experiments were treated with a weak solution of nitre, equivalent to 4·0095 grams of nitric anhydride, the soil also containing nitrates equivalent to 0·8440 gram of nitric anhydride. The soil was placed in a flask of ten litres capacity, to which was fitted a disengagement tube opening under mercury. During the first five days absorption took place, the mercury rising to a height of 80 mm. in the tube, owing, perhaps, to absorption of oxygen by organic matter and of carbon dioxide by carbonates. The tension of the gas in the flask then increased, till in a fortnight it was again equal to that of the atmosphere. Ten days afterwards a violent disengagement of gas took place, which overturned the measuring vessel. The volume of gas evolved could not therefore be ascertained. Gas was given off for about a month after this; the composition of the gas and the amount of nitric anhydride and of ammonia in the soil was then ascertained. The soil contained about five litres of gas, which consisted almost entirely of carbon dioxide and nitrogen, the weight of the tubes for the detection of nitrogen oxides and hydrocarbons not varying by more than 2 milligrams in each case. The nitric anhydride in the soil had entirely disappeared and the ammonia had increased by 101 milligrams, or only 6·6 per cent. of the equivalent of the nitric anhydride originally present. It is concluded therefore that the great bulk of the nitric anhydride had been reduced to nitrogen.

In a second experiment the sample of soil which was employed in the last experiment, and which was therefore free from nitrates, was placed in the flask with the same quantity of nitre as before. An absolute vacuum, allowance being made for tension of water-vapour, was then established in the flask. After remaining in this state for one day, a volume of air containing at 0° and 760 mm. pressure 3873·2 c.c. of nitrogen, was introduced. The absorption and disengagement took place as in the last experiment, save that, in this case, loss was prevented. The gas in the flask was then pumped out and analysed, as well as that obtained by spontaneous disengagement. The first portion of gas from the flask contained 14·8 per cent. of carbon dioxide. This proportion went on gradually increasing till it amounted to nearly 100 per cent. It is supposed that this was due to the decomposition of the bicarbonates, as the pressure of the carbon dioxide decreased. The nitric anhydride in the soil had, as before, disappeared, and had not been replaced by an equivalent quantity of ammonia. The proportion of the latter was however 15·3 per cent. of the theoretical equivalent, or more than twice as great as in the last experiment. The nitrogen collected amounted to 4897·9 c.c., or 4·2 per cent. *more* than the nitrogen of the nitre and air introduced. This excess of nitrogen

must have been set free from the organic matter during the combustion of the latter. B. J. G.

Action of Gaseous Ammonia on Nitrate of Ammonia.

By F. M. Raoult (Compt. rend., lxxvi, 1261—1262).

This paper gives the author's results of the action of gaseous ammonia on nitrate of ammonia, which are almost identical with those published a short time ago by E. Divers (*Proc. Roy. Soc.*, xxi, 109, and *Jour. Chem. Soc.*, xxvi, 598). The author, however, states that the crystals, which separate on exposing the liquid to the air, are a compound of one equivalent of ammonia with one of ammonium nitrate; these part with the whole of the ammonia by prolonged exposure. He also notices that the aqueous solution of ammonia dissolves more ammonium nitrate than pure water does, and that the quantity of ammonia absorbed by an aqueous solution of the nitrate is somewhat greater than that absorbed by pure water. C. E. G.

Hygroscopic Character of Monocalcic Phosphate.

By K. Birnbaum (Deut. Chem. Ges. Ber., vi, 898—901).

The author, as well as Erlenmeyer, has found that monocalcic phosphate when kept in air saturated with moisture absorbs a large quantity of water, which, however, according to Erlenmeyer, is completely given off when the salt is exposed to the open air. The author's experiments do not confirm this. Monocalcic phosphate is a hygroscopic salt, which, when kept in the air, contains varying quantities of water, the amount of which is proportional to the amount of moisture in the air. Novana superphosphate behaves in the same way. On analysing these substances, the water must, therefore, be determined, which is easily done by mixing them with freshly ignited lime and igniting the mixture. C. S.

Antique Bronze. By E. Reichardt (Arch. Pharm. [3], ii, 516).

Some fragments of rings or ornaments found near Danzig gave the following results on analysis; the fragments were covered with the ordinary green film of oxide, or *patina*:—

Specific gravity	7·12
Tin	5·591
Silver	traces
Iron	0·363
Lead	0·041
Zinc	1·388
Copper	92·638
	100·021

On comparison with several other analyses published at different times by Kopp, Terreil, Church, Arnandes, Struve, and Olivier, great differences are noticeable in the quantities of tin, zinc, and lead present in the various specimens. C. R. A. W.

On some Properties of Gypsum. By A. Cossa (Gazzetta chimica italiana, iii, 185—188).

The power of gypsum to augment the fertility of soils may doubtless be ascribed in great measure to its property of facilitating the decomposition of complex rocks containing alkaline silicates, and thereby bringing the alkalis into a condition favourable to their ready absorption by the roots of plants.

To estimate the intensity of this decomposing action, the author has compared the quantity of matter dissolved, in a given time and within given ranges of temperature, from various rocks by a saturated solution of gypsum, with the quantities dissolved out of the same rocks under similar conditions by pure distilled water. He finds that 1000 parts of pure water dissolve 2·19 parts of pure crystallised gypsum at 16·25° and 2·352 at 22°, numbers agreeing nearly with those obtained by other experimenters.

The rocks were reduced to very fine powder and left for twenty days in contact with a saturated solution of gypsum at temperatures ranging from 16° to 22°. The results are given in the following table, together with those obtained in like manner with pure water:—

	Matter dissolved out.	
	By pure water.	By a saturated solution of gypsum.
	Per cent.	Per cent.
Gneiss, containing undecomposed orthoclase and potash-mica	0·125	0·463
Trachyte, decomposing, from Monte Chioja, Vicenza..	0·0937	0·2562
Trachyte, undecomposed, from Monte Ortona (Euganian Hills)	0·0571	0·138
Trachyte, porphyroidal, decomposing (containing sanidine, mica, hornblende), from San Pietro Montagnone (Euganian Hills)	0 0567	0·0927
Trachyte from San Daniele	0·0750	0·1630
Granite (albite, quartz, mica), from Montorfano, Lago Maggiore	0·0727	0·207
Granite (orthoclase, mica containing a trace of lithia, quartz), from Baveno, Lago Maggiore	0·0996	0·2875
Felspar, white, compact, in veins in Diorite: from Mosso, Biella	0·350	0·714
Basalt, compact, of Monte Nuovo (Euganian Hills) ..	0·1271	0·304
Perlite, from Monte Siena (Euganian Hills)	0·0624	0·1982

The solvent action exercised by gypsum on rocks containing alkaline silicates may perhaps give rise to the presence of potash, soda, and lithia in certain mineral waters, especially in sulphuretted waters.

H. W.

Observations on the Influence of Metallic Deposits on Zinc in presence of Acids and Alkalis: new Heliographic Methods. By C. GOURDON (Compt. rend., lxxvi, 1250—1254).

M. MERGEL's researches (*Compt. rend.*, lvi, 693, 868) have shown that zinc, on which any metal of the last three groups has been precipitated, is attacked by nitric acid only on the uncovered portions, whilst sulphuric acid, hydrochloric acid, acetic acid, &c., on the contrary attack only those portions which are covered. Zinc partly covered with a thin layer of precipitated platinum is attacked and dissolved at those parts by sulphuric acid diluted with 7000 times its volume of water. With gold it is attacked by an acid diluted with 5000 parts of water; copper requires an acid diluted with 4000 volumes, silver 3500 volumes, tin 1500 volumes, antimony 700 volumes, bismuth 500 volumes, and lead 400 volumes. The action is irregular with mercury, the spot gradually enlarging, and the zinc being dissolved only at the edges of the spot. The arsenites, arsenates, and antimonates also give spots which promote the solution of the zinc, but the action is less energetic. Deposits of cobalt, nickel, and iron, on the contrary, are comparable with those of platinum in their action, indeed cobalt causes the solution of the zinc by sulphuric acid diluted with 10,000 times its volume of water.

The author also finds that salts of the same base, but with different acids, yield deposits which do not behave in the same way, the chlorides giving deposits which are more active than those produced by the sulphates, which in their turn excel those of the corresponding nitrates. Moreover, salts rendered slightly alkaline by the addition of ammonia give a more active deposit than the salts themselves; ferrous sulphate, for instance, produces no deposit by itself, but on adding ammonia a very active one is formed. Zinc thus covered with a metallic deposit is also readily attacked by alkalis. The author is of opinion that these phenomena cannot be attributed to the action of electricity alone; but that they are partly due to the rugosity of the zinc, produced by the action of the salt.

The reactions above described may be applied to a new kind of heliography.

1. If a photographic picture be laid on a plate of zinc, the metallic silver by which the picture is produced will be transferred to the plate, forming a metallic deposit, which will facilitate the attack of the zinc by an acidulated liquid. The author has employed potassium cyanide for this purpose, although it presents certain inconveniences. 2. The second process, so far as the necessary preliminary operations are concerned, is founded on the property possessed by certain varnishes employed in the carbon photographic process, of drying up in sunshine, or again, of remaining dry in the dark and becoming pitchy on exposure to light. These varnishes being applied on the paper, the parts which remain or become moist after exposure to light behind a positive or negative photograph, are alone capable of retaining the active powders, which are applied to the surface by means of a brush.

C. E. G.

Mineralogical Chemistry.

The Corundum of North Carolina, Georgia, and Montana, and the Minerals accompanying it. By L. Smith (Compt. rend., lxxvii, 357—359; 439—442).

The corundum of North Carolina (U.S.) appears in the form of blue, green, grey, pink, ruby-coloured, or white masses, sometimes weighing 300—400 kilograms. Some specimens show a cleavage plane, and some have a hexagonal prismatic form. The gangue is either chrysolite or serpentine. The former occurs in a system of veins extending for 190 miles. Their course for 130 miles lies along the north-west side of the Blue Mountains, at a mean distance of ten miles from the summit, from Mitchell County to Macon County. They then make a curve round the source of the Little Tennessee, and run towards the north-west for ten miles, after which they follow the line of the Blue Mountains. The serpentine appears at intervals along the whole of this line. From Mitchell to Macon it is always found inclosed in gneiss containing rose-garnet, kyanite, and pyrites. After the above-named curve it is found in both gneiss and hornblende. From Buck's Creek to the south-west the latter occurs in very large masses, in which albite replaces the ordinary feldspar. Associated with the serpentine are chalcedony, magnetic oxide, chrome-iron, spinelle, rutile, chromite, chlorite, talc, steatite, anthophyllite, tourmaline, emeryllite, epidote, zoisist, albite, asbestos, picrolite, actinolite, and tremolite. The corundum occurs sometimes in ripidolite in the fissures of the serpentine, sometimes, as at Buck's Creek, in chlorite, except the red variety which is found in zoisist. The chrysolite of North Carolina holds an analogous position to that of the calcareous rock of Asia Minor which forms the gangue of emery in that region. The adjacent rocks in each of the localities show the formations to be of the same geological age, and contemporaneous with the formation in Chester (Mass.). Each locality has, however, its special characteristic. In Asia Minor the emery is associated with but a small quantity of black tourmaline. Diaspore is also rare, but when it does occur it is found in most perfect crystals. The emery of Naxos and Nicaria is accompanied by black tourmaline in abundance. The rock containing the corundum of Chester is composed of talc and saponite with hornblende-gneiss. It is accompanied by magnetic oxide and tourmaline in abundance.

In the second note on the subject, it is stated that Prof. Shepard is in possession of two crystals of corundum, each weighing 150 kilograms. One of these is red on the surface and bluish-grey in the interior. Its form is that of a hexagonal prism whose summit is terminated by a rather uneven hexagonal plane. The second crystal is greyish-blue, with a pale sapphire colour near the angles. Its form is that of a regular hexagonal prism, well defined at one end only. Some of the lateral faces are coated with pearly margarite. Crystals smaller than the above are often transparent at the ends. Some of the minerals accompanying corundum in this locality have been newly examined.

Diaspore is not associated with corundum in North Carolina. Chlorite is found in several varieties, differing somewhat in composition. Two specimens, (1) in large plates, (2) a friable variety contained:—

	SiO_2.	Al_2O_3.	Fe_2O_3.	MgO.	H_2O.
(1.)	27·00	21·60	16·63	22·00	12·30 = 99·53
(2.)	29·15	10·50	23·50	25·44	10·04 = 98·63

Margarite (emeryllite), which accompanies emery in Asia Minor, and the presence of which in Chester led to the discovery there of that mineral, abounds in North Carolina. Its composition is—

SiO_2.	Al_2O_3.	CaO.	Na_2O.	H_2O.
32·41	51·31	10·98	2·43	2·13 = 99·26

The following results were obtained in analysing, (1) a green, (2) a black variety of zoisist. The numbers are put in comparison with (3) the composition of zoisist from the Lake of Geneva:—

	SiO_2.	Al_2O_3	Fe_2O_3.	CaO.	MgO.	Na_2O.	Cr_2O_3.	H_2O.	
1.....	45·70	24·01	4·56	13·44	8·03	2 91	0 52	0·60	= 99·77
2.....	45·90	13·34	11 46	12·20	12·53	3·39	?	0·66	= 99·48
3.....	43·59	27·72	2 61	21 00	2·40	3·08	?	?	= 100·40

Andesite, which occurs in a granular state, gave the following numbers on analysis:—

SiO_2.	Al_2O_3.	Na_2O.	CaO.	Fe_2O_3.
64·12	24·20	9·28	2·80	0·14 = 100·54

A large quantity of the more perfect small pieces of blue or ruby-coloured corundum are cut, polished, and sold as precious stones. Pebbles of greenish corundum, resembling those found in the East in the neighbourhood of rubies, have been found in large quantities on the sand banks near the source of the Missouri, which are being worked for gold.

B. J. G.

A Compact Anglesite from Arizona (U.S.). By G. J. Brush (Amer. Jour. Sci. [3], v, 421).

This mineral is associated with galena in the Castle Dome district. The unoxidised galena sometimes forms a nucleus, but in other cases it has entirely disappeared, the anglesite being arranged in continuous elliptical or circular bands similar to those sometimes seen in agate. The transition in colour, due to the progressive oxidation, from the central black galena to the greyish-white or colourless and transparent anglesite, is often very gradual. The sp. gr. of the light variety is about 6, while in some of the dark varieties it is 6·44. Hardness = 3. Analysis showed that a specimen might be dark and yet contain but 0·2 per cent. less lead sulphate than the light variety, the mean amount

being 98·83 per cent. The difference in colour is caused by the remaining one per cent., which in the dark specimens is almost entirely made up of lead sulphide, while in the light variety it is chiefly clay. The anglesite contains only half as much silver as the galena.

B. J. G.

Calcium Borate from Oregon (U.S.). By A. W. Chase (Amer. Jour. Sci. [3], v, 287—290).

This mineral occurs on the Lone Ranch farm, in the maritime county of Curry, the northern boundary of California. The country in the vicinity is a succession of terraces, the top layers of which are talcose slate, and serpentine. Further inland is a high range of mountains, one peak of which, called Red Mountain, situated five miles from the sea, is at the head of the stream on the banks of which the borate was found. The outcrop was first observed at a point 500 yards from the sea, and close to a crater-like formation. Being an excellent material for polishing silver, the mineral is being extracted in large quantities. The main vein of borate was met with in a bed of blue steatitic rock, near its junction with overlying slate. It was in the form of pounded masses with corrugated sides and depressed tops. These were of a pretty uniform size, and weighed about 200 pounds each. They were arranged in a continuous line. These masses are very pure. Their colour is milk-white, and they have a greasy feel. The following is the analysis of (I), the hard borate in veins; (II) the softer kind in boulders:—

	H_2O.	CaO.	Chlorides.	Alkalis.	B_2O_3.
I.	25·00	29·80	?	trace	45·20 = 100·00
II.	22·75	29·96	trace	0·25	47·04 = 100·00

The mineral is, therefore, a hydrated calcium borate. Its appearance does not coincide with that of any variety described by Dana. It is probable that the boric acid was evolved, in the form of vapour, from a hot spring; that it then passed through a layer of calcium carbonate; and, holding the carbonate in suspension, it penetrated the liquid mud which ultimately formed the stratum of clay. As the mud cooled, it pressed the borate into such shapes as those in which it is found, the vapours that escaped being retained in the fissures of the slate and forming the present veins.

B. J. G.

Kjerulfin, a New Mineral from Bamle in Norway. By F. v. Kobell (J. pr. Chem. [2], vii, 272—275).

This mineral occurs massive, with imperfect cleavage in two directions nearly at right angles to one another. Fracture uneven and splintery. Lustre fatty. Colour pale red; translucent in thin fragments. Specific gravity 3·15. Hardness 4—5. Exhibits weak white phosphorescence

on warming. Fusibility about 3; melts with some intumescence to a blistered enamel. Easily soluble in hot concentrated hydrochloric acid; somewhat less easily in nitric acid. With sulphuric acid it evolves hydrofluoric acid, while calcium sulphate separates. The result of analysis was :—

P_2O_5.	MgO.	CaO.	Na_2O.	Fl.	SiO_2.	Al_2O_3.	
42·22	37·00	7·56	1·56	4·78	1·50	5·40	= 100 02

with traces of potassium, iron, and sulphuric acid.

When the non-essential constituents are deducted, this composition corresponds with the formula $2Mg_3(PO_4)_2 + CaFl_2$, a small portion of the calcium being replaced by sodium.

Kjerulfin differs from wagnerite, which it resembles in many respects, by containing less fluorine and sodium, and more calcium, so that its solution in hydrochloric acid gives a precipitate with sulphuric acid, which is not the case with wagnerite.

M. J. S.

Wagnerite. By F. v. KOBELL (J. pr. Chem. [2], vii, 275—278).

THE analyses of this mineral by Fuchs and Rammelsberg agree best with the formula $Mg_3(PO_4)_2 + MgFl_2$. A specimen from Radelgraben near Werfen in Saltzburg has been examined by v. Kobell. It occurred in closely packed parallel prisms, with deep vertical striation. The prismatic angle measured 120°—121°. Cleavage imperfect.

The fusibility was about 3·5, or rather lower than stated by Fuchs: this might perhaps be due to a somewhat larger amount of iron. It was soluble, though slowly, in hydrochloric, nitric, and sulphuric acids. The analysis gave—

P_2O_5.	MgO.	CaO.	$Na_2O + K_2O$.	Fe_2O_3.	Al_2O_3.	Fl.	H_2O.	
40·30	32·78	2·24	5·12	8·00	1·11	10·00	0·50	= 100·05

from which the composition of the essential portion of the mineral would appear to be $2Mg_3(PO_4)_2 + \left.\begin{matrix}\frac{2}{3}\text{Na}\\ \frac{1}{3}\text{Ca}\end{matrix}\right\}Fl_2$, the double atom, Na = 46, replacing Ca isomorphously.

The presence of the alkalis appears to have been overlooked by both Fuchs and Rammelsberg.

M. J. S.

Hygrophilite, a New Mineral of the Pinite Group.

By H. LASPEYRES (J. pr. Chem. [2], vii, 278—294).

A MINERAL occurring in the sandstones of Halle on the Saale, and found principally in the workings of the royal coal mine of Wettin. Though presenting points of similarity to many known species, it yet differs in some respects from all. It occurs in small, irregular, isolated nodules or veins of a dull greenish colour, much resembling litho-

marge. It is not however amorphous, but exhibits a microscopic cryptocrystalline scaly structure. The individual scales exhibit a distinct cleavage parallel to their planes. They also show double polarisation, and give interference colours which change as the analyser is rotated. When highly magnified, the body of the substance appears homogeneous, colourless and transparent, but filled with innumerable spherical vesicles, each of which is covered with a greenish skin. A few microscopic crystals of pyrites were the only impurity observable. The mineral in mass is translucent at the edges only; its lustre and streak are fatty, like those of talc; its fracture even and finely splintery; its general structure schistose; hardness 2—2·5; specific gravity 2·67. It feels greasy and adheres strongly to moist bodies. On heating, it decrepitates and gives off much water; if gently ignited it blackens, but without becoming much harder; strong ignition changes its colour to a pale red or yellow, and increases its hardness to 4—5. It is rather less fusible than natrolite, and gives a blistered enamel. Placed in contact with water it rapidly exfoliates, with evolution of gas, to a soft whitish mud. In no other liquid, except ammonia, does this take place. Strong ignition deprives it of this property.

Its most remarkable character is its hygroscopic power. The air-dried powder already contains 9 per cent. of water, of which it loses 1·85 per cent. over calcium chloride, 4½ per cent. at about 300°, and the whole on strong ignition. After drying at 300°, it is capable of absorbing gradually, during about 30 days, 22·8 per cent. of water when placed in air saturated with aqueous vapour at about 16°. At the same time it expands considerably, but without altering its appearance under the microscope. The saturated substance parts with its water with great facility when placed over calcium chloride, and appears to lose about 1·4 per cent. more than could be removed by the same method from the air-dried powder. After being partially sintered by strong ignition, it absorbed only about 2 per cent. of water during 18 days' exposure to damp air.

The mineral is completely decomposed by hot hydrochloric acid, with separation of flocculent silica. In boiling potash it is all dissolved except the trace of pyrites.

Two analyses of the air-dried substance, one made on the solution obtained by imperfect decomposition with hydrochloric acid, and the other by fusion with alkaline carbonate, agreed well, showing that the mineral is homogeneous.

The mean results gave—

Si.	Al.	Fe.	Ca.	Mg.	K.	Na.	H.	O.	
22·60	17·06	2·54	·82	1·03	4·71	1·01	1·05	1·90	= 102·67

which leads to a rather complicated formula corresponding only approximately with—

$$2(RO.SiO_2) + 3(Al_2O_3.2SiO_2) + 5H_2O;$$

but if the sum of the bases be calculated into their hydrogen equivalent it will be seen that the composition may be referred with great exact-

ness to the hydrated silicic acid, H_4SiO_4, the difference amounting to only 0·208 per cent. of water in excess. The chief difficulty is that, to obtain this formula, the 9 per cent. of water in the air-dried substance, more than a third of which is lost in dry air, must be taken into account. The author, however, considers that this is no hindrance to the view he proposes, especially since many substances, silicic hydrate amongst them, lose their so-called water of constitution under similar circumstances.

The characters which distinguish hygrophilite from all other minerals are—1st. Its complete solubility in potash; 2nd. Its solubility in hydrochloric acid; 3rd. Its behaviour with water and moist air; 4th. Its low specific gravity, the only other mineral of a similar specific gravity being kilinite, which is much harder and insoluble in hydrochloric acid, &c.

M. J. S.

Fibrous Quartz from South Africa, a Pseudomorph after Crocidolite. By F. WIBEL (Jahrbuch f. Mineralogie, 1873, 367—380).

THE brown fibrous quartz from the Orange River, analysed by Klaproth, is a mixture of pure white fibrous quartz with göthite ($Fe_2O_3.H_2O$), which may be dissolved out by hydrochloric acid. Blue fibrous quartz is essentially a mixture of white fibrous quartz with crocidolite. Both varieties are pseudomorphs after crocidolite, the brown being the product of a slow and complete transformation, the blue of an incomplete and rapid transformation. The amount of alteration in each case is shown by the following analyses:—

	Asbestos-like crocidolite, from the Cape. Stromeyer.	Brown fibrous quartz. F. Wibel.	Blue fibrous quartz. F. Wibel.
SiO_2	50·81	57·46	97·27
FeO	33·88*	Fe_2O_3 37·56	FeO 1·67
MnO	0·17	—	—
MgO	2·32	—	—
CaO	0·02	—	0·15
Na_2O	7·03	—	0·15
H_2O	5·58	5·15	0·76
	99·81	100·17	100·00

In the formation of the brown fibrous quartz, the decomposition of the crocidolite mass appears to have been accompanied by an almost simultaneous washing out of the soda, magnesia, &c., and by an oxidation and hydration of the ferrous oxide. The 33·88 p. c. FeO of the original crocidolite is exactly equivalent to the 37·56 p. c. Fe_2O_3 of the brown fibrous quartz. This shows that no iron has been carried away by the decomposing liquid, the whole of it having been oxidised

* Equivalent to 37·62 Fe_2O_3.

in situ, and deposited as göthite, $Fe_2O_3.H_2O$; and consequently that the circulation of the decomposing liquid and of the products of decomposition must have been very slow.

This slow decomposition, indeed, has enabled the delicate fibres of crocidolite, while undergoing so complete a change of composition, to retain their form instead of being converted into a dense structureless mass of quartz. On the other hand, in the more rapid action which has produced the blue fibrous quartz, nearly all the ferrous oxide has been carried away, together with the other monoxides, leaving quartz together with about 2·5 p. c. of unaltered crocidolite.

These conclusions are confirmed by the microscopic examination of thin sections of the two varieties. The brown variety exhibits, both in longitudinal and in transverse sections a complete and tolerably uniform impregnation with ferric hydrate, each individual fibre appearing more or less brown. In the blue mineral, on the other hand, a longitudinal section exhibits a white homogeneous matrix traversed by blue or sometimes brownish fibres, with sharp edges, running parallel to one another at various distances, and of various diameters; and in accordance with this, the transverse section appears as a snow-white substance dotted with dark points. Under the polarising microscope, the white mass exhibits double refraction with brilliant play of colours.

The blue quartzes which accompany crocidolite in a few other localities (Golling in Salzburg, Rudka in Moravia, &c.), must also be regarded, not as primary quartzes coloured by crocidolite, but likewise as secondary products resulting from an incomplete but very rapid decomposition of that mineral. The same is true with regard to the blue iron ore of Klaproth. Quartz, indeed, in spite of its prismatic habit, appears to be incapable of *originally* assuming the fibrous form of aggregation.

H. W.

Nefediewite; a New Mineral. By P. Pusirewsky (Jahrbuch f. Mineralogie, 1873, 420).

This amorphous mineral, very much like lithomarge, occurs, together with fluorspar, in the limestone of Nertschinsk. Hardness = 1·5. Sp. gr. = 2·335 at 18°. Fracture, conchoidal; colour, white, inclining to rose-red; opaque, but translucent on the edges; somewhat unctuous to the touch. Water dissolves 0·2 p. c. of it, the mineral crumbling to pieces, and the solution exhibiting an alkaline reaction. Over sulphuric acid, it gives off water (11·13 p. c. in 22 days), and the dried mineral absorbs water again from the air. It loses 19·13 p. c. of its weight at 250°, and 4·73 p. c. more when heated to fusion. It is scarcely soluble in acids. The analyses give very discordant results, but the mean numbers agree most nearly with the formula, $H_6MgAl_2Si_5O_{17}$, or $3H_2O.MgO.Al_2O_3.5SiO_2$.

H. W.

Analysis of Andesite from Czibles in the Gutin Range of North Transylvania. By G. TCHERMAK (Min. Mittheil., 1872, iv, 261).

THIS rock belongs to the augitic andesites; it contains large lamellæ of plagioclase and small light green prisms of diallogite, imbedded in a dense, greyish-green ground mass. Sp. gr. = 2·773. Analysis gave—

SiO_2.	Al_2O_3.	Fe_2O_3.	FeO.	MnO.	MgO,	CaO.	K_2O.	Na_2O.	H_2O.	CO_2.	
56·56	21·67	2·41	2·57	trace	2·12	8·52	2·10	2·53	1·14	0·37	= 99·99

H. W.

Wolynite. By J. MUSCHKETOW (Jahrbuch f. Mineralogie, 1873, 422).

THIS name is given to a porphyritic rock first observed by Ossowsky near the village of Michailowka, on the shore of the Grosdowitz in Volynia. It consists essentially of a dark-coloured to black hornblende and a triclinic felspar, with magnetic iron ore and iron pyrites as secondary constituents. Its porphyritic character is determined by the felspar. The hornblende occurs in irregular groups of needle-shaped crystals, distinctly cleavable in the longitudinal direction. The felspar gave the oxygen ratio—

$$SiO_2 : R_2O_3 : (R'',R'_2)O = 1 : 2·61 : 7·29,$$

which, taking into consideration the partially decomposed state of the mineral, points distinctly to oligoclase. This felspar exhibits peculiar aggregations similar to those of spherical diorite (Kugel-diorite), but more ellipsoidal.

Muschtekow regards this rock as belonging to the porphyrite family, and observes that the name *wolynite* should be retained only in case of the spheroïdal arrangement of the felspar proving to be characteristic of it; in the contrary case this name should be discarded, and the rock regarded as porphyrite.

H. W.

The Basalt and Hydrotachylyte of Rossdorf, Darmstadt. By TH. PETERSEN (J. pr. Chem. [2], vii, 152—158).

THIS basalt is interesting from the number of minerals occurring in it. It contains, amongst others, augite, olivine, nephelin, titaniferous iron, apatite, a plagioclastic felspar, leucite, mica, &c. Calcium carbonate is also found in it, and it includes especially obsidian-like tachylyte and hydrotachylyte.

Among the products of its decomposition are osteolite and zeolites.

Analyses are given of tachylyte, tachylytic glass, and hydrotachylyte.

G. T. A.

Analyses of the Gases evolved from the Volcano of Nisiros. By H. GORCEIX (Compt. rend., lxxvii, 597—601).

THE gases collected during March, 1873, from the fumeroles in the crater had the following composition:—

	a.	*b.*		*c.*			*d.*
Hydrogen sulphide..	65·0	74·0	77·0	74·0	71·7	70·0	8·6
Carbon dioxide......	30·0	21·6	18·0	21·6	24·0	25·3	90·2
Oxygen............	0·4	0·4	0·4	0·4	0·4	0·4	—
Residue............	4·6	4·0	4·6	3·7	3·9	3·8	1·2

a was from the older group of fumeroles: the residue was incombustible. *b* and *c* were from two apertures in the more recent group, the analyses being made at intervals of three days: the residue was combustible. *d* was from a solfatara in the island of Cos: the residue consisted of nitrogen.

The fumeroles are surrounded by deposits of sulphur, and the soil is impregnated with sulphuric acid.

Since March the volcano has entered into eruption.

M. J. S.

On the Gases from the Springs at Inselbad (Paderborn), and their Application to Inhalation. By E. v. MEYER (J. pr. Chem. [2], vii, 181—190).

THERE are two springs from which gases are given out; one of these, the Badequelle, is unenclosed. Two analyses of the gases from it gave the following results:—

CO_2	1·61	1·48
O	7·33	7·38
N	91·06	91·14
	100·00	100·00

The other spring, the Hauptquelle, from which the gases for inhalation are obtained, is carefully closed in. The temperature of the water is 17·5°—18°, that of the air at the time being 7·5°. It contains more carbonic acid than the Badequelle.

Analyses of specimens of air taken from the room used for inhalation at intervals during a period of 70 minutes give results which differ but very slightly in percentage composition from atmospheric air. The medicinal properties of the air may be due to its excessive dampness, or to the small quantity of salts contained in it. The origin of the gases is explained on the supposition of Bischof, that atmospheric air, passing down through the deeply fissured chalk-marl, and in contact with carbonaceous matter, is robbed to a great extent of its oxygen. The carbon dioxide produced is partly dissolved in the water of the spring and partly escapes among the free gases.

G. T. A.

Analysis of the Carlsquelle at Helmstedt. By R. FRESENIUS (J. pr. Chem. [2], vii, 191—199).

THE water of this spring, which has been known since the middle of the eighteenth century, appears in the well itself somewhat turbid, owing to the ochry flocculi suspended in it. If a glassful is taken out, it is at first quite clear, but soon becomes opalescent from the oxidising action of the air upon the dissolved ferrous carbonate.

The taste of the water is mildly ferruginous. At first there is no smell, but if a flask half filled be shaken up, a slight odour of sulphuretted hydrogen is perceptible.

The temperature of the spring, October 11, 1872, was 15°, that of the air being 11°. The specific gravity of the water at 20° is 1·0000381, and the quantity yielded by the spring is 10 litres in a minute.

The quantitative composition is as follows, the carbonates being calculated as simple carbonates:—

	In 1,000 parts by weight,
Sodium chloride	0·026189
Sodium nitrate	0·003126
Ammonium nitrate	0·000593
Potassium nitrate	0·011244
Potassium sulphate	0·004740
Calcium sulphate	0·017350
Basic calcium phosphate	0·000679
Aluminium phosphate	0·000021
Barium sulphate (traces of strontium)	0·000143
Calcium carbonate	0·006650
Magnesium carbonate	0·007440
Ferrous carbonate	0·018553
Manganous carbonate	0·000251
Silicic acid	0·009183
Resinous organic matter	0·000389
Humus-like ,,	0·003451
Total of solid constituents	0·110002
Carbon dioxide, combined with carbonates as bicarbonate	0·013956
Carbon dioxide, perfectly free	0·083968
Sulphuretted hydrogen, traces	—
Nitrogen, small quantity	—
Total of all constituents	0·207926

A second analysis follows with the carbonates calculated as anhydrous bicarbonates. In other respects it is the same as the above.

The action of the spring is due to the dissolved ferrous carbonate, which it contains, compared with other chalybeate springs in moderate quantity; but, owing to the very small amount of free carbonic acid and dissolved salts of the alkalis and alkaline earths, the action of the iron is not interfered with, as in the case of other springs of a similar nature.

G. T. A.

Analysis of River Mud.

By POTT (Landw. Versuchs-stationen, xvi, 196—198).

THE dried mud of a little river near Aachen had the following composition:—

Water	8·60
Combustible matter (containing nitrogen ·408)	9·18
Ash	82·22
	100·00

Concentrated hydrochloric acid dissolved from 100 parts of the mud:—

CaO.	MgO.	K_2O.	Na_2O.	P_2O_5.	SO_3.	SiO_2.
·658	·153	·226	·076	·366	·509	·094

R. W.

Organic Chemistry.

Action of Platinum and Palladium on Hydrocarbons.

By J. J. COQUILLION (Compt. rend., lxxvii, 444—446).

THE action of platinum made red-hot and plunged into the vapours of alcohols and ethers, which then keep up the incandescence, is believed by the author to extend to all hydrocarbons, volatile oils, bodies similar to aniline, &c., but not to the fixed oils, or sulphuretted essential oils. The products of the imperfect combustion have been, in every case yet examined, the aldehyde or acid, or both, analogous to the substance experimented upon. The apparatus employed was modified in different cases, but it consisted essentially of a tube containing the incandescent platinum wire, through which was passed a mixture of air and the vapour, the products being collected in a condenser connected with an aspirator. Toluene treated in this manner yielded bitter almond-oil, which, on exposure to air, was converted into benzoic acid. Marsh-gas did not maintain the incandescence unless the wire was heated by the pile till the action had fairly commenced. Davy found, it is true, that the wire suspended above the flame of his safety-lamp remained red hot after an explosion of marsh-gas, but it is believed that this was due to the presence of other hydrocarbons. The product of the reaction started by the pile is formic acid; no aldehyde could be obtained. Ethylene-vapour, if allowed to pass very slowly over the platinum, keeps the latter red-hot without an explosion taking place, acetic acid being formed. Many other metals act in the same way as platinum, but on account of their melting when heated in a flame, the experiment is difficult to make. Palladium is a better agent in partial oxidation than even platinum. Marsh-gas keeps it red-hot without the aid of the pile. It is also safer than platinum; no instance occurred of its causing ethylene to explode. Other peculiarities of this metal are that

it becomes wrinkled on the surface, is rendered brittle, and diminishes in weight, after a few days' employment in the above experiments.

B. J. G.

A New Hydrocarbon from Vegetable Fats.

By J. König and J. Kiesow (Deut. Chem. Ges. Ber., vi, 500).

In a former communication the authors have shown that the fat-waxes from various kinds of hay and straw contain larger percentages of carbon than those possessed by the highest known fatty ether, viz., myricyl melissate, $C_{60}H_{120}O_2$; they now find that these substances are mixtures of *cholesterin* and a new hydrocarbon, giving on analysis—

Carbon...... 84·96 Hydrogen...... 15·28,

agreeing best with the formula, $C_{20}H_{42}$, but not improbably consisting of *cerotene*, $C_{27}H_{54}$. The hydrocarbon was isolated by treating the crude fat wax with benzoic acid in a sealed tube for 18 hours at 200°, whereby cholesteryl benzoate was formed insoluble in warm alcohol, the filtrate depositing flakes on cooling; these were dried in contact with caustic potash to remove benzoic acid, and the dry mass exhausted with ether: the hydrocarbon thus dissolved out melted at 65°—66°, and solidified at 65 8°—65°; but this product was possibly not perfectly pure, retaining a trace of cholesterin.

C. R. A. W.

Dipropargyl. By L. Henry (Deut. Chem. Ges. Ber., vi, 955—963).

When diallyl tetrabromide is distilled with a large excess of caustic potash or soda, it loses two molecules of hydrobromic acid, and *dibromodiallyl*, $C_6H_8Br_2$, is formed, some of which, by the further loss of hydrobromic acid, is converted into dipropargyl. Dibromodiallyl is a limpid liquid, possessing a bitter and pungent taste, and peculiar smell. It has the spec. grav. 1·656, and boils at 205°—210°. It combines most readily with bromine, and, when heated with a solution of caustic potash in absolute alcohol, is converted into *dipropargyl* or *diallylenyl*, C_6H_6. This isomeride of benzene is a mobile, limpid liquid, having a high refractive index, and an odour like that of propargyl ether, but more intense and penetrating. It boils at about 85°, has at 18° the spec. grav. 0·81, and burns with a luminous and smoky flame. It is easily distinguished from benzene by its property of combining with explosive violence with bromine, forming the tetabromide, $C_6H_6Br_4$, a viscid liquid, having a faint smell and bitter taste. It has at 19° the spec. grav. 2·460, and when heated it gives off hydrobromic acid, and leaves a carbonaceous residue. It combines in the dark with more bromine, forming probably the octobromide, $C_6H_6Br_8$. Dipropargyl gives, with an ammoniacal solution of cuprous chloride, a greenish-yellow precipitate, which, when dried over sulphuric acid, or at 90°—100°, has the composition $C_6H_4Cu_2 + 2H_2O$. It explodes at about 100°, and when touched with a flame, burns with a scintillant green flame. The silver-compound, $C_6H_4Ag_2 + 2H_2O$, is obtained as an *amorphous* white precipitate, by adding the hydrocarbon to an *aqueous*

solution of silver nitrate; in the light it soon becomes pink, and then black. It explodes below 100°, leaving a residue of carbon and silver. The constitution of dipropargyl or diallylenyl may be expressed by the formula, $CH—C—CH_2—CH_2—C—CH_2$, which explains why it forms compounds containing two equivalents of a metal, while in allylene, $CH—C—CH_3$, only one atom of hydrogen can be replaced. In a former communication the author pointed out that the propargyl-compounds boil 18°—20° higher than the corresponding allyl-compounds; dipropargyl ought, therefore, to boil at about 95°—100°, but it boils at 85°. Diallyl makes, however, a similar exception, for while the allyl-compounds boil at the same temperature as the normal propyl-compounds, the hydrocarbon boils at the same temperature as di-isopropyl, or 10° lower than normal dipropyl.

C. S.

Action of Ethyl Chloride on Sulphuric Anhydride.

By TH. V. PURGOLD (Deut. Chem. Ges. Ber, vi, 502).

THE author has already shown that the chief product of this action is *chloro-sulphuric ether*, $C_2H_5.O.SO_2.Cl$; he now finds that simultaneously there are produced substances which, by the action of water, give rise to isethionic and chlorisethionic acids, separable by treating the mixed solution of these barium salts with alcohol, whereby barium chlorisethionate, $Ba(C_2H_4ClSO_3)_2.2H_2O$, crystallises out on standing: whence he infers that, simultaneously with chlorosulphuric ether, there are produced two bodies isomeric therewith, namely, $C_2H_4\left\{\begin{matrix}Cl\\SO_2.OH\end{matrix}\right.$ and $C_2H_4\left\{\begin{matrix}OH\\SO_2.Cl\end{matrix}\right.$; the production of the latter, however, is uncertain, as the isethionic acid obtained from the bye-products might be obtained, not from the body, $C_2H_4\left\{\begin{matrix}OH\\SO_2\,Cl\end{matrix}\right.$, by the action of water, but from the body, $C_2H_4\left\{\begin{matrix}Cl\\SO_2.OH\end{matrix}\right.$ by the action of the carbonate employed to neutralize the mixed acids; or it might result from the further action of sulphuric anhydride on chlorosulphuric ether, the author finding isethionic acid to be actually producible in this way.

The substance termed chlorosulphuric ether is found to be identical with the product of the action of phosphorus pentachloride on potassium ethylsulphate; Willm has also found, in the author's laboratory, that the same body is produced by the action of fuming sulphuric acid on chlorocarbonic ether. Under a pressure of six lines, the ether distils almost perfectly at 80°—96°.

Ammonia acts violently on chlorosulphuric ether, apparently forming ammonium chloride and ethyl sulphamate, $SO_2\left\{\begin{matrix}NH_2\\O.C_2H_5\end{matrix}\right.$; the latter, however, was not obtained pure. Toluidine does not give a better result. Phenol gives rise to a clear liquid, which evolves ethyl chloride and hydrogen chloride at 60°, forming products not yet investigated.

C. R. A. W.

Monochloracetal. By E. Paternò and G. Mazzara (Gazzetta chimica italiana, iii, 254—256).

This compound, which Lieben obtained in 1838 among the products of the action of chlorine on aqueous alcohol, and afterwards (1864) in a purer state by the action of sodium ethylate on dichlorethyl oxide, may be prepared more easily and in considerable quantity by treating this ether with absolute alcohol. For this purpose the portion of the product of the action of dry chlorine on anhydrous ether which boils between 130° and 150° is mixed with twice its volume of absolute alcohol, and boiled for seven or eight hours in a flask with reversed condenser. The product is then treated with water; the oil which separates is dried over calcium chloride and distilled; and the distillate is twice rectified.

The product thus obtained is pure monochloracetal, $C_6H_{13}ClO_2 = C_2H_3Cl(OC_2H_5)_2$. It is a colourless, transparent liquid, of agreeable odour, sweetish and burning taste. It boils at 156·8° (corr.), and its specific gravity referred to that of water at 4° is 1·0418 at 0°, 1·0416 at 26·3°, and 0·9315 at 99·9° It is decomposed by zinc at the boiling heat, giving off ethyl chloride, and leaving a mixture of ethyl alcohol and unaltered chloracetal.

Dichlorethyl oxide treated with alcoholic potash, or sodium ethylate in dilute solution, likewise yields monochloracetal. H. W.

Commercial and Pure Isobutyl Alcohol and Isobutyraldehyde. By G. A. Barbaglia (Deut. Chem. Ges. Ber., vi, 910—914).

The commercial isobutyraldehyde which the author used for his former experiments was, as he now finds, a mixture containing a large quantity of acetone, probably derived from isopropyl alcohol contained in the commercial isobutyl alcohol.

To prepare pure isobutyl alcohol, the crude compound is converted into the potassium xanthate, which is three times crystallised from alcohol, and then decomposed by dilute sulphuric acid. The pure alcohol thus obtained gave on oxidation no acetone, which was shown by the fact that on treating the dry compound with chlorine and then with water and concentrated potash, it was not coloured crimson.

C. S.

Constitution of some Glycerin Derivatives. By W. Hartenstein (J. pr. Chem. [2], vii, 295—318).

Epicarbhydric acid was prepared by the method of Pazschke (*J. pr. Chem.* [2], i, 97), strong boiling hydrochloric acid being employed instead of sulphuric acid for the decomposition of the epicyanhydrin.

With the view of ascertaining whether acetyl chloride can attach itself to epicarbhydric acid to form the compound $\begin{matrix} CH_2.COHO \\ CH.(C_2H_3O.O), \\ CH_2Cl \end{matrix}$ this acid was heated to 140° with acetyl chloride for several hours. No new compound was, however, obtained, and attempts to obtain

compounds of epicarbhydric acid with acid sodium sulphite or hydrochloric acid were equally unsuccessful. Epichlorhydrinic acid was not changed by treatment with hydrochloric acid and tin, or with sodium amalgam, but when it was heated to 160° with strong hydriodic acid, it became converted into normal butyric acid. This fact tends to confirm Erlenmeyer's formula, $\begin{matrix} CH_2 \\ CH \\ CH_2Cl \end{matrix}\!\!>O$, for epichlorhydrin. If this formula is the true one for epichlorhydrin, we should expect epicarbhydric acid, $\begin{matrix} CH_2 \\ CH \\ CH_2CO.OH \end{matrix}\!\!>O$, to yield the chloride of dichlorbutyric acid on treatment with phosphorus chloride, but an experiment in this direction did not lead to definite results. Moreover, if we assume that epichlorhydrin has the above constitution, it follows that dicarbhydric acid should yield a propylene oxide having the constitution $\begin{matrix} CH_3 \\ CH \\ CH_2 \end{matrix}\!\!>O$ on distillation with lime. On performing the experiment, a gas was obtained which was absorbed by hydrochloric acid, with formation of a compound having an odour resembling that of camphor. The author considers it probable that this gas consists of the body sought, and Carstanjen intends to continue the investigation of this substance.

When dichlorhydrin is allowed to drop on phosphoric anhydride contained in a retort, an energetic reaction takes place, and on cautiously distilling the product, a distillate is obtained which consists of dichlorhydrin and a colourless liquid passing over at 109°. It burns with a bright smoky flame fringed with green, is insoluble in water, miscible with alcohol or ether, and has a specific gravity of 1·233 at 17·5°. This substance possesses the composition of an *allylene dichloride*, and it is probably formed as follows:—

$$\begin{matrix} CH_2Cl \\ CHHO \\ CH_2Cl \end{matrix} - H_2O = \begin{matrix} CH_2Cl \\ C \\ CH_2Cl \end{matrix}$$

When this allylene chloride is exposed to the action of chlorine, a tetrachloride, $\begin{matrix} CH_2Cl \\ CCl_2 \\ CH_2Cl \end{matrix}$, is formed. It is a colourless liquid, having a penetrating odour like that of turpentine and a burning taste. Alcohol and ether dissolve it readily, and its specific gravity is 1·503 at 17·5°. The corresponding *dibromide of allylene dichloride* is produced under analogous circumstances, and forms a colourless, somewhat viscid liquid, boiling at 212°, and having an odour and taste like that of the tetrachloride. Its specific gravity is 2·083 at 17·5°.

Sodium acts on the above-mentioned allylene dichloride, or on its solution in benzene, and liberates the corresponding allylene, which was found not to precipitate ammoniacal silver solution. This leads the author to represent this modification of allylene by the formula $\begin{matrix} CH_2 \\ C \\ CH_2 \end{matrix}$,

and it tends to support the formula $\begin{matrix} CH_2Cl \\ CHHO \\ CH_2Cl \end{matrix}$ for dichlorhydrin.

When the above-mentioned allylene is passed into bromine, a solid substance, crystallising from it in leaflets, and melting at 195°, is formed. This is doubtless a modification of allylene tetrabromide.

T. B.

Action of Oxalic Acid on Polyatomic Alcohols. By LORIN (Compt. rend., lxxvii, 363—365).

THE oxalines (see this Journal [2], xi, 1122) of ethene and octene alcohols, of mannite, dulcite, erythrite, and quercite have been obtained, and oxamide precipitated from them on addition of ammonia. Neither glucose nor sugar of milk forms oxalines. The monatomic alcohols appear to be but partially converted into oxalines by oxalic acid, since ammonia produces only a slight turbidity in the resulting product.

B. J. G.

The Constitution of Suint. By E. SCHULZE (J. pr. Chem. [2], vii, 163—178).

THE portion of suint which dissolves in alcohol amounts to 10 or 15 per cent. of the whole, and this portion has been proved to contain some of its cholesterin in a free state.

In a previous paper (p. 513 of this volume) the author alluded to a substance formed during the saponification of suint and crystallising from acetone or ether in needles, or separating from alcohol in flocks or jelly-like masses. This substance, which is isomeric with cholesterin and is called by the author *isocholesterin*, was obtained by digesting its benzoate with alcoholic potash. It separates from absolute alcohol in flocks when the solution is dilute, but a concentrated alcoholic solution solidifies to a translucent jelly. When isocholesterin is evaporated with nitric acid and afterwards treated with ammonia, it gives the same reaction as cholesterin, but when it is treated with hydrochloric acid and iron chloride, or sulphuric acid and chloroform, it does not react like cholesterin. Isocholesterin, like cholesterin, is slightly soluble in cold alcohol, but easily soluble in hot alcohol or ether. Hot acetic acid dissolves it readily, and flocks of an unstable compound of isocholesterin and acetic acid are deposited on cooling. This compound loses its acetic acid on fusion. Isocholesterin melts at 137°—138°, and solidifies, on cooling, to a brittle vitreous mass. A mixture of cholesterin and isocholesterin melts at a lower temperature than either separately; one such mixture melted at 136°. *Isocholesteryl benzoate* has been already alluded to (*loc. cit.*). It melts at 190°—191°, is very slightly soluble in alcohol, more soluble in hot acetone, and still more easily soluble in ether, from which it separates in microscopic needles. *Isocholesteryl acetate* was obtained by digesting isocholesterin with acetyl chloride until the evolution of hydrochloric ceased, and then heating the mixture to 100° in a sealed tube. On removing the excess of acetyl chloride by evaporation, isocholesteryl

acetate was obtained as an amorphous substance, melting below 100°, and easily soluble in alcohol. *Isocholesteryl stearate* was obtained by heating isocholesterin with stearic acid to 200°. The product melted at 72°, and separated from ether in microscopic needles which dissolved to a small extent in hot alcohol and separated from it in flakes.

Phosphorus pentachloride converts isocholesterin into a yellow resinous mass, easily soluble in ether, and slightly soluble in alcohol. Analysis led to the formula, $C_{26}H_{43}Cl$.

The author's researches show that the portion of suint which does not dissolve in alcohol consists of ethers of cholesterin and isocholesterin, and the nature of the acids contained in these ethers will form the subject of future investigations. The portion soluble in alcohol contains free cholesterin and probably free isocholesterin; also fatty ethers of both these substances.

Apparently a third alcohol, less rich in carbon than cholesterin, is contained in the insoluble portion of suint, and although all attempts to isolate this alcohol were fruitless, the author believes that he has distinguished crystals of its benzoate in the mixed benzoates, and as the insoluble portion of suint contains only 77·84 per cent. of carbon, while cholesterin oleate and stearate require about 81 per cent., it is probable that either excess of acid is present, or that the mixture contains a notable proportion of the third alcohol.

That portion of suint which is soluble in water contains, as is well known, a considerable proportion of potassium salts, which probably arise from the saponification of the cholesterin salts. This perhaps accounts for the presence of free cholesterin. T. B.

Monobromacrylic Acid from β-Dibromopropionic Acid.

By R. WAGNER and B. TOLLENS (Deut. Chem. Ges. Ber., vi, 512).

WHEN β-dibromopropionic acid (obtained by addition of bromine to allyl alcohol, forming dibromopropylic alcohol, and oxidation of the latter) is heated with excess of alcoholic caustic potash, it splits up, forming potassium bromide and monobromacrylate, easily separable by crystallisation, the former being much the most soluble. From pure potassium monobromacrylate the free acid is obtainable as a crystalline mass by souring with sulphuric acid, agitating with ether, and evaporating the ethereal extract to dryness. It melts at 69°—70°, and decomposes before it reaches the boiling point. The authors attribute to this substance the formula—

$$\begin{array}{l} CH_2 \\ CBr \\ COOH. \end{array}$$

β-dibromopropionic acid being $\begin{array}{l} CH_2Br \\ CHBr \\ COOH \end{array}$, so that there is probably a parallelism between

β-dibromopropionic acid and propylene dibromide,
α-dibromopropionic acid and methyl-bromacetol,
Bromacrylic acid and bromopropylene.

Monobromacrylic acid combines with hydrobromic acid when digested at 100° with the fuming aqueous acid; the product is identical in fusing point, 63°—64°, and crystalline form with the original β-dibromopropionic acid. C. R. A. W.

Electrolysis of Citraconic and Mesaconic Acids.

By G. Aarland (J. pr. Chem. [2], vii, 142—146).

In a former paper the author described the action of the electric current on a concentrated solution of potassium itaconate. In the present paper the investigation is extended to potassium citraconate and mesaconate. The gases developed at the positive pole only were examined. The results were as follows:—

Potassium itaconate is decomposed, with formation of allylene and carbon dioxide. The allylene is not absorbed by a silver solution, but completely by bromine. In the residue, acrylic and mesaconic acids were detected with certainty.

Potassium citraconate gives carbon dioxide and an allylene containing an atom of hydrogen replaceable by metals. In addition, acrylic and mesaconic acids were found with tolerable certainty. Potassium mesaconate gives carbon dioxide and allylene, which is precipitated by a silver solution. The other products of the decomposition are probably acrylic and itaconic acids.

The formula of the three allylenes is not decided, but the one obtained from itaconic acid is not identical either with ordinary allylene or with those obtained from citraconic and mesaconic acids.

G. T. A.

On Monochloritamalic Acid. By T. Morawski (J. pr. Chem. [2], vii, 158—162).

The author, at the request of Professer Gottlieb, was induced to examine the behaviour of itaconic acid when treated by the same method by which monochlorcitramalic acid is produced from citraconic acid. Excess of chlorine was passed into sodium itaconate, hydrochloric acid added, and the liquid evaporated to dryness in a retort on the water-bath. The residue was treated with ether, and after some difficulty the acid was obtained from the ethereal extract in the crystalline form.

The composition of monochloritamalic acid is represented by the formula $C_5H_7ClO_5$; it differs from monochlorcitramalic acid in forming very much smaller crystals, and in giving no crystalline precipitate with barium acetate, even when the solution is very concentrated. It forms salts with difficulty, chiefly because of its proneness to decomposition in the presence of bases.

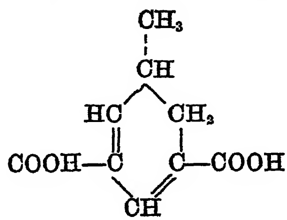
G. T. A.

Action of Phosphoric Chloride on Pyroracemic Acid. By C. Böttinger (Deut. Chem. Ges. Ber., vi., 893—896).

When pure pyroracemic acid is treated with phosphoric chloride, a violent reaction takes place; this was modified by external cooling, and

on distilling the product, a liquid passing over between 55°—60° was obtained. When this fluid was treated with alcohol a liquid having the odour of acetic ether was produced. In another instance, pyroracemic acid was added to phosphoric chloride cooled in a frigorific mixture, and after the action had terminated the product was treated with alcohol. Under these circumstances ethyl chloride and carbonic anhydride were evolved, and on distilling the product acetic ether passed over. The residue in the retort was treated with water, which caused the separation of an oil which was found to be the ethyl-dichlorpropionate of Climenko, and ether extracted from the aqueous solution separated from this oil, a small quantity of an acid which was perhaps pyroracemic acid or hydrovinic acid.

Preliminary Notice on a New Acid from Pyroracemic Acid.—The behaviour of pyroracemic acid and of its basic barium salt towards water at a temperature of 130° has already been studied by the author, and he has now investigated the action of water on pyroracemic acid partly neutralised with baryta. For this purpose 10 grams of pyroracemic acid and 6 grams of barium hydrate were heated with water to 130° for more than six hours. A magma of shining crystals was thus obtained, and these crystals were found to consist of an acid slightly soluble in water, melting at 133°, and volatilising completely when heated on platinum-foil. Analysis showed it to contain 2 atoms more of hydrogen than uvitic acid. The author represents it by the following formula:—



T. B.

Sulphuretted Chloro-carbonic Ethers. By F. SALOMON (J. pr. Chem. [2], vii, 252—258).

THE author first points out the possibility of producing very numerous groups of isomerides connected more or less directly with the sulphocarbonates, and differing from one another in the position occupied by the sulphur. Three sulphuretted chlorides, for example—

$$\mathrm{CO}{}^{\mathrm{SC_2H_5}}_{\mathrm{Cl}} \qquad \mathrm{CS}{}^{\mathrm{OC_2H_5}}_{\mathrm{Cl}} \qquad \mathrm{CS}{}^{\mathrm{SC_2H_5}}_{\mathrm{Cl}}$$

are derivable from ethylchlorocarbonate, and by replacing the chlorine by NH_2 three corresponding amides may be obtained. One of these is xanthamide, $\mathrm{CS}{}^{\mathrm{OC_2H_5}}_{\mathrm{NH_3}}$.

A second, corresponding with the first of the three formulæ above given has been obtained by the author, and is described further on.

The number of cases of isomerism among the metallic sulphocarbonates would be much greater were it not for the tendency of the sulphur to unite with the metal. This isomerism may, however, be studied in the ethers containing two different alcohol-radicals, to one or other of which the sulphur may be attached.

The author having already obtained carbonyl-disulpho-diethyl, $CO\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$, by the action of phosgene on sodium mercaptide, was led to expect the formation of an intermediate product by the action of the same gas upon mercaptan. This expectation was fulfilled. Mercaptan saturated with phosgene slowly evolves hydrochloric acid, and yields on distillation a colourless, strongly refractive liquid, which irritates the eyes and has a smell slightly resembling that of mercaptan. Boiling point 136°; specific gravity 1·184 at 16°. This body is carbonylsulphethyl chloride, $CO\begin{matrix}SC_2H_5\\Cl\end{matrix}$.

By treatment with potassium ethylate it gives carbonyl-oxysulpho-diethyl—

$$CO\begin{matrix}SC_2H_5\\Cl\end{matrix} + C_2H_5OK = CO\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix} + KCl,$$

and by the action of sodium mercaptide it furnishes, by a similar reaction, carbonyl-disulpho-diethyl, $CO\begin{matrix}SC_2H_5\\SC_2H_5\end{matrix}$.

Acted upon by aqueous or alcoholic ammonia the chloride furnishes a crystalline body containing no sulphur, the purification of which is difficult and has not been carried further by the author. Ammonia gas, however, produces a different reaction, resulting in the formation of an amide, $CO\begin{matrix}SC_2H_5\\NH_2\end{matrix}$, already referred to.

The introduction of the atom of S in place of the O of the oxethyl-group in phosgene ether is accompanied, as observed in other cases (this Journal, p. 620), by a rise of 40° in the boiling point.

The following differences are also to be noticed in the specific gravities:—

$$\left.\begin{matrix}CO\begin{matrix}OC_2H_5\\OC_2H_5\end{matrix} = \cdot975\\ CO\begin{matrix}SC_2H_5\\OC_2H_5\end{matrix} = 1\cdot0285\end{matrix}\right\}\begin{matrix}\text{Diff.}\\ \cdot0535\end{matrix} \qquad \left.\begin{matrix}CO\begin{matrix}OC_2H_5\\Cl\end{matrix} = 1\cdot13\\ CO\begin{matrix}SC_2H_5\\Cl\end{matrix} = 1\cdot184\end{matrix}\right\}\begin{matrix}\text{Diff.}\\ \cdot054\end{matrix}$$

W. A. T.

Dichloracetone. By A. Theegarten
(Deut. Chem. Ges. Ber., vi, 897).

The author has repeated Mulder's experiments (this Journal, [2], xi, 379), and obtained dichloracetone.

This body has no caustic properties, and combines with the acid sulphites of the alkali-metals.

C. S.

Ethyl Sulphocyanate. By V. Meyer and C. Wurster (Deut. Chem. Ges. Ber., vi, 965).

By the action of ethyl iodide on silver sulphocyanate no ethylsulphocarbimide is formed, but ethyl sulphocyanate boiling at 141°—142°, and not at 146° as generally stated. Ethyl sulphocyanate prepared by the ordinary method boiled at the same temperature, when water boiled at 99°.

C. S.

Action of Acetic Anhydride on Ammonium Sulphocyanate. By M. Nencki and W. Leppert (Deut. Chem. Ges. Ber., vi, 902—905).

When ammonium sulphocyanate is heated with acetic anhydride or glacial acetic acid on a water-bath, gases consisting of prussic acid, carbonyl sulphide, and a little hydrogen sulphide and carbon disulphide are given off, and *acetyl-persulphocyanic acid*, $C_2H(C_2H_3O)N_2S_3$, is formed. It is almost insoluble in cold water, sparingly soluble in boiling water, more freely in alcohol and ether. It crystallises in brilliant yellow needles and has a slightly acid reaction. Ammonia dissolves it without alteration, but caustic alkalis readily decompose it. It forms with most metals compounds which are amorphous precipitates, and decompose on drying in a vacuum. Only the copper salt, $2[C_2H(C_2H_3O)N_2S_3]_2Cu + CuO$, showed a constant composition; it is obtained as an olive-green precipitate, changing rapidly into red, by adding copper sulphate to a very dilute ammoniacal solution of the acid.

When ammonium sulphocyanate is boiled with acetic anhydride, sulphur separates out, carbon sulphide distils over, and acetamide is left behind.

Acetyl-persulphocyanic acid, when heated with iron-powder and dilute acetic acid, forms at first a blue solution, which soon becomes colourless and now contains *sulphur-urea*.

When ammonium sulphocyanate is fused with benzoic acid, it yields hydrogen sulphide and benzonitril. By heating acetyl-sulphur-urea with water and mercuric cyanide, acetyl-urea and mercuric sulphide are formed.

C. S.

Isomeric Series of Benzene Derivatives. By V. v. Richter (Deut. Chem. Ges. Ber., vi, 879—882).

Meyer has assumed that when bromobenzoic acid or sulphobenzoic acid is fused with sodium formate, the carboxyl group replaces the bromine or the sulpho-group. The above researches of the author tend however to prove that the bromine or sulpho-group is replaced by nascent hydrogen evolved from the melted formate, and that the benzoic acid thus reproduced is acted on by nascent carboxyl. The author has now proved that bromobenzoic acid is reduced to benzoic acid by fusion with potash; and Meyer has detected benzoic acid among the

products of the action of sodium formate on sulphobenzoic acid. Although Meyer did not detect terephthalic acid among the products of the action of sodium formate on bromobenzoic acid, the author finds that, as in the case of benzoic acid, terephthalic acid is formed.

The reactions which take place on fusing benzoic acid or its derivatives with sodium formate, apparently depend to a great extent on the fusibility of the mixture; for example, the easily fusible potassium sulphobenzoate can yield pure isophthalic acid on fusion with sodium formate, while the less fusible potassium bromobenzoate or benzoate yields both isophthalic acid and terephthalic acid. In the case of the sodium salts no reaction takes place.

Although these experiments do not disprove Meyer's assumption that the carboxyl-group takes the place of the bromine in bromobenzoic acid, or the sulpho-group in sulphobenzoic acid, they show that the evidence on which Meyer's assumption is made, is not of any weight in the question.

T. B.

Benzyl-toluene. By PLASCUDA and TH. ZINCKE (Deut. Chem. Ges. Ber., 906—910).

THIS hydrocarbon, prepared by acting with zinc on a mixture of toluene and benzyl chloride, is a mixture of two isomerides, yielding by incomplete oxidation two ketones and two benzyl-benzoic acids.

β-Benzoyl-benzoic acid is more soluble in hot water than the α-acid, and crystallises in long broad needles, or by slow evaporation in well-defined, oblique prisms, containing 2 mol. of water and melting at 85°—87°; the anhydrous compound melts at 127°—128°. Its salts appear to be all freely soluble; the ethylic ether forms glistening prisms melting at 58°.

The mixture of ketones does not solidify, even after weeks, but by adding to it a crystal of solid tolylphenyl ketone (which the authors obtained from Merz), a magma of needles was formed and thus the two modifications could be separated. The solid compound boils, if the column of mercury be completely surrounded by the vapour, at 326·5°, and is identical with the compound obtained by Merz and Kollaritz (this Journal [2], xi, 1035). The liquid compound boils at 313°—314°, and appears also to be identical with the liquid tolylphenyl ketone of these chemists.

Besides these bodies, a high-melting acid and some anthraquinone were formed, which were probably derived from some other hydrocarbon contained in the benzyl-toluene.

C. S.

Synthesis of Diphenylmethane. By V. MEYER and C. WURSTER (Deut. Chem. Ges. Ber., vi, 963).

THIS hydrocarbon is produced in quantity by acting on a mixture of benzyl alcohol and benzene with sulphuric acid, which is diluted with glacial acetic acid according to Baeyer's method. Besides diphenyl-

methane, other hydrocarbons, boiling above 300° are formed, which are undoubtedly identical with those obtained by Zincke and Baeyer in analogous syntheses.

C. S.

Fluorene. By BARBIER (Compt. rend., lxxvii, 442—444).

BERTHELOT (*Ann. Chim. Phys.* [4], xii, 222) discovered in the portion of coal-tar distilling at 300°—340°, a very fluorescent substance, to which he gave the name of *fluorene*, without attributing any definite formula to it. It is best obtained by modifying his method so far as to make the first crystallisation of the portion distilling at 300°—305° from a mixture of alcohol and benzene. By this operation a small quantity of acenaphthene is separated, and the melting point is raised to 112°, that is to say, 7° higher than when the substance is crystallised from alcohol only. After another crystallisation from pure alcohol, the hydrocarbon melts at 113°. The composition of fluorene is represented by the formula $C_{13}H_{10}$. *Dibromofluorene*, $C_{13}H_8Br_2$, obtained by acting on fluorene with bromine, occurs in beautiful clinorhombic tables, the following angles of which have been observed:—

$$m : m = 97° 40'; \ p : m = 97° 58'; \ p : h = 102° 10'; \ p : a^1 = 131°;$$
$$h^3 : h^3 = 132° 42'; \ p : h^3 = 94° 55'.$$

When it is brought to a red heat in presence of lime, dibromofluorene yields a hydrocarbon melting below 100°, and having the odour and appearance of diphenyl. Fluorene is, therefore, probably a diphenyl methylene, and may be formulated thus—$C(C_6H_5)_2$. *Fluorene picrate* crystallises in fine red needles, melting at 80°—82°. Its formula is, $C_{13}H_{10}.C_6H_3(NO_2)_3O$.

B. J. G.

Oil of Lemon. By A. OPPENHEIM (Deut. Chem. Ges. Ber., vi, 915—917).

ALTHOUGH oil of turpentine and oil of lemon differ in their physical and chemical properties, they yield identical cymenes, which on oxidation yield paratoluic acid and terephthalic acid. The cause of the isomerism of these terpenes, as probably of many others, can therefore be only the different position of the double linking of the carbon-atoms in these hydrocymenes.

C. S.

Essential Oil of Roman Camomile. By E. DEMARÇAY (Compt. rend., lxxvii, 360—363).

GERHARDT considered this substance to be a mixture of angelyl hydride, some resinous matter, and a hydrocarbon boiling at 175° and isomeric with turpentine-oil, to which he gave the name of camomillene. The author, however, finds it to be a mixture of several ethers, chiefly the angelate and valerate of butyl and amyl. It does not give off hydrogen

when treated with potash as Gerhardt supposed. The result of the reaction is the formation of potassium angelate and valerate, together with butyl and amyl alcohols. It is preferable to use potassium ethylate. After agitation with this the oil is left for 36 hours. An equal volume of water is then added, and the liquid is distilled. When potassium carbonate is added to the distillate, the latter is divided into two layers. The upper layer, after being dried in contact first with solid potassium carbonate and then with anhydrous baryta, is separated by fractional distillation into two alcohols. The first of these, boiling at 107°—109°, yields butyl iodide boiling at 119°—121°. The second, boiling at 129°—132°, yields amyl iodide boiling at 144°—146°. Neither ethyl nor propyl alcohol is formed by the action of potash on the oil. The products of the reaction which boil at a higher point than amyl alcohol are a mixture of this last and other alcohols. The alcohols escaped Gerhardt's notice, probably because he dried his products over calcium chloride, which combines with alcohols. His percentages of carbon and hydrogen in the oil are believed to be too high from want of proper purification. The oil, like other ethers, combines with metallic chlorides.

B. J. G.

Derivatives of Cymene. By F. LANDOLPH (Deut. Chem. Ges. Ber., vi, 936—938).

WHEN cymene from camphor is heated with nitric acid of specific gravity 1·4 at 40°—50°, it yields two mononitro-products. That which is produced in comparatively large quantity is a pale-yellow liquid having a faint smell like that of cymene, and at 18° the specific gravity 1·0385. It is decomposed by heat, and yields by oxidation a nitrotoluic acid, which is very sparingly soluble in cold water, a little more freely in hot water, and crystallises from dilute alcohol in small needles or plates. It differs from the common nitrotoluic acid by subliming without previous fusion. The barium salt is very soluble in water and crystallises in slender needles grouped in stars. The second nitrocymene crystallises from alcohol in stellar needles melting at 124·5°.

C. S.

Identity of the Cymenes from Camphor, Ptychotis-oil and Thymol. By F. FITTICA (Deut. Chem. Ges. Ber., vi, 938—943).

BY oxidising these three hydrocarbons with strong red nitric acid, they are converted into mononitrotoluic acid melting at 189°—190°, a small quantity of common toluic acid being formed at the same time. Nitric acid of specific gravity 1·4 converts them into the two nitrocymenes described in the preceding paper. The cymene from thymol was prepared by distilling this compound with phosphorus pentasulphide; at the same time some thiocymene was formed, which appears to be isomeric with that from camphor. It is a liquid boiling at 233°—235° and having the specific gravity 0·989. The mercuric salt forms rhombic, greenish crystals, and the lead salt crystallises from

hot alcohol in golden-yellow needles. On oxidation it yields a sulphotoluic acid, which is insoluble in water and sparingly soluble in alcohol, and crystallises in yellowish needles melting at 190°.

C. S.

Oxycymene from Camphor. By A. Fleischer and A. Kekulé (Deut. Chem. Ges. Ber., vi, 934—936).

By the action of iodine on camphor, Claus obtained, besides camphin, camphoretin, and colophene, a small quantity of a yellowish oil smelling like creasote. But neither he nor Schweizer, who repeated these experiments, could obtain this camphocreasote in quantity sufficient for analysis. The following modification of Claus' method yields a larger quantity of this compound. Camphor is heated with about one-fifth of its weight of iodine in a vessel connected with a reversed condenser, and the product submitted to distillation, until the temperature of the vapour is 170°. The residue is treated with concentrated soda-lye, which leaves a resinous body undissolved, and the filtrate is shaken repeatedly with ether. On adding hydrochloric acid to the filtrate, the cymophenol separates out; it is an oily liquid, which does not solidify at —20°, and boils at 231°—232°. By the action of phosphorus pentasulphide, it is converted into cymene, and a thiocymene which is identical with that obtained by distilling camphor with phosphorus pentasulphide.

This oxycymene is identical with that which Pott and Müller prepared from cymene-sulphonic acid, and also with the so-called *cavacrol* from oil of caraway.

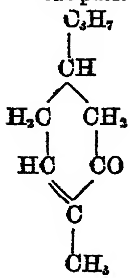
The distillate which was obtained after treating camphor with iodine contains a considerable quantity of the hydrocarbon, which Claus called camphin. On standing over night, it solidified into a magma of crystals having the composition $C_{10}H_{16}O + HI$. This additive product is very deliquescent, and fumes strongly in the air.

C. S.

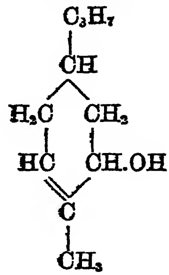
Constitution of Camphor. By A. Kekulé (Deut. Chem. Ges. Ber., vi, 929—934).

The constitution of this compound has been often discussed, but chemists do not agree whether it is an alcohol, a phenol, an aldehyde, or a ketone, although at present it is assumed by most that it belongs to the latter class of bodies. Several graphic formulæ have been proposed, but neither of them explains all the reactions of this singular body. In order to do this, we must in the first place take into consideration that it is an indifferent body; secondly, that by combining with hydrogen, it is converted into borneol, which possesses the character of an alcohol; and thirdly, that alkalis transform it into monobasic campholic acid, and oxidizing agents into bibasic camphoric acid. We must also remember that, by abstraction of the elements of water it is readily converted into cymene, an aromatic hydrocarbon, containing methyl and propyl (or isopropyl) in the para-position. All these reactions are readily explained by the following formulæ:—

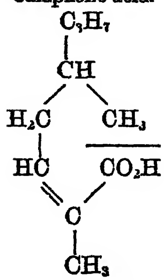
Camphor.



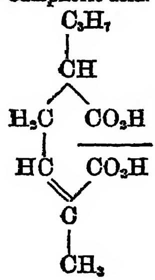
Borneol.



Campholic acid.



Camphoric acid.



In assuming these formulæ, it must be stated that the positions of the radicals, CH_3 and C_3H_7, are known, but those of the oxygen and of the double-linked carbon-atoms must at present be left undecided.

Camphor is therefore a kind of ketone, and borneol the corresponding secondary alcohol, the formation of which from camphor is similar to that of other secondary alcohols from their ketones, although it takes place under somewhat different conditions. In the formation of campholic acid and camphoric acid, the linking of two carbon-atoms is severed, that which was combined with oxygen being converted into carboxyl, while the other, under the influence of alkalis, combines with hydrogen, whereas real oxidizing agents also convert it into carboxyl.

The transformation of camphor into cymene is a complicated reaction, intermediate products being formed, varying with the dehydrating agent used. Such a compound is thiocymene, which is produced by the action of phosphorus pentasulphide.

C. S.

Researches on Santonin. By S. Cannizzaro and F. Sestini (Gazzetta chimica italiana, iii, 241—251).

Santonic acid, $C_{15}H_{20}O_4$.—This acid is formed by the prolonged action of hot alkaline solutions on santonin ($C_{15}H_{18}O_3$). 50 grams of crystallised santonin are gradually added, with agitation, to 500 grams of a boiling saturated solution of barium hydrate, whereupon a white amorphous mass is deposited, consisting of the barium salt of santonin (which may

be called *barium santonite*). The liquid with the precipitate is boiled for about 12 hours in a flask, with reversed condenser, whereby the santonite is gradually converted into santonate, which dissolves, the liquid acquiring a yellow colour. Into this yellow solution, after cooling (and dilution with water if barium hydrate has crystallised out), a stream of carbonic anhydride is passed as long as a precipitate is formed; the liquid is heated, filtered, and mixed with sulphuric acid, which precipitates barium sulphate, together with the greater part of the santonic acid; and the precipitate is collected on a filter, washed, dried, and treated with alcohol, which dissolves the santonic acid, together with a small quantity of yellow resinous matter. The alcoholic solution is evaporated, the residue treated with ether, and the resulting ethereal solution filtered and evaporated, whereupon it deposits santonic acid in fine large crystals, which have a faint yellowish colour, but may be obtained perfectly colourless by one or two fractional crystallisations from ether. For complete purification the product must be further crystallised by cooling from alcohol diluted with an equal bulk of water.

Santonic acid is colourless, and is not affected by the solar rays, which quickly turn santonin yellow. It is slightly soluble in cold water (100 pts. water at 17° dissolve 0·559 pt.), more soluble in hot water, from which it separates in prismatic crystals, very soluble in ether, still more in alcohol, moderately soluble also in chloroform and glacial acetic acid, very sparingly in carbon sulphide.

The crystals of santonic acid are orthorhombic, exhibiting the combination, $\bar{P}\infty . \breve{P}\infty . 0P$, the macrodome generally predominating. Axes, $a : b : c = 0{\cdot}4589 : 1 : 0{\cdot}6544$; angle $0P : \bar{P}\infty = 114° 39'$; $0P : \breve{P}\infty = 123° 12'$. Cleavage easy parallel to the faces $\breve{P}\infty$.

Santonic acid melts at 161°—163° (santonin at 170°), to a colourless liquid, which crystallises to a white mass on cooling, but often exhibits the phenomenon of super-fusion. Fused santonic acid undergoes alteration at a temperature not exceeding 170°, turning brown, and giving off an odour like that of some of the pyrogenous products of santonin. With alcohol and caustic potash, it does not give the fine violet-red colour which is characteristic of santonin.

Santonates.—Santonic acid has a very decided acid reaction, and decomposes carbonates with brisk effervescence when the solution is heated with them. It is monobasic. The *sodium-salt*, $C_{15}H_{19}NaO_4$, separates from a solution concentrated to a syrup and placed over sulphuric acid, as an amorphous, transparent or vitreous mass, having a faint straw-yellow colour; but by open evaporation over the water-bath, it is obtained in radiate or stellar groups of needles. It is deliquescent, very soluble in water and in alcohol; soluble also in ether containing alcohol. The *silver-salt*, $C_{15}H_9AgO_4$, obtained by precipitating the barium salt with silver nitrate, is white, but alters on exposure to light. It may be washed on a filter with cold water, in which, however, it dissolves somewhat freely. The *barium-salt*, $(C_{15}H_9O_4)_2Ba$, is very soluble in water, but may be obtained in crystals by evaporating its concentrated solution over sulphuric acid. It is not precipitated from its aqueous solution by alcohol; but on adding a mixture of alcohol with a little ether to its concentrated aqueous solution, it sepa-

rates in delicate needle-shaped crystals, which remain for a long time suspended in the liquid.

Santonites—This term is applied by the authors to the metallic derivatives of santonin, $C_{15}H_{17}RO_3$, originally called *santonates* by Heldt, who first examined them (*Ann. Chem. Pharm.*, lxiii, 10, 40). Cannizzaro and Sestini find that when sodium santonite, which, according to Heldt, contains four molecules of crystallisation-water, is heated above 100°, it is converted, by assimilation of the elements of one molecule of water, partly into santonate, partly into a substance having a red colour changing to brown.

Santonin bromide, $C_{15}H_{18}Br_2O_3$, is formed on adding bromine to a solution of santonin in chloroform, or in glacial acetic acid. It is best prepared by means of the latter solvent the bromine being added in molecular proportion ($Br_2 = 160 : C_{15}H_{18}O_3 = 246$). After two or three hours the bromine-compound separates in fine, red, needle-shaped crystals, which must be collected on a well dried double filter, washed four or five times with glacial acetic acid, pressed in the filter between two glass plates, then within several folds of thoroughly dried paper, placed between bricks, and squeezed in a press, and finally dried over sulphuric acid or sticks of potash.

This compound dissolves with red colour in ether and in acetic acid; it emits a faint odour of bromine, absorbs water from the air, and quickly alters, yielding hydrogen bromide and a red-brown, amorphous substance. When heated in the water-bath it first gives off bromine, then suddenly turns brown, and gives off large quantities of hydrogen bromide. In contact with water, it gives up its bromine in a few seconds, colouring the water yellowish-red, and the solution is decolorised by potash, with formation of hydrobromic acid and a white residue possessing all the properties of santonin.

From these reactions it may be inferred that the red compound is a brominated addition-product of santonin, although, on account of the difficulty of purifying it, the numbers obtained by analysis do not agree very closely with the formula, $C_{15}H_{18}Br_2O_3$ (35·24 and 35·42 p. c. bromine, instead of the calculated quantity of 39·41).

Action of Nascent Hydrogen on Santonin.—Santonin treated with water and sodium amalgam containing 3 p. c. sodium, gradually dissolves, forming a strongly alkaline liquid, which, when treated after cooling, with very dilute sulphuric acid, yields a white flocculent precipitate, which may be washed with cold water, dried by pressure between paper, and finally over sulphuric acid.

This white substance is soluble in ether, very soluble in alcohol, sparingly in water, and separates from these solvents in the amorphous state, with yellow colour and resinous aspect. Between 80° and 90° it becomes somewhat viscid; at 100° it turns yellow, and may be drawn out into threads, becoming hard and friable on cooling; between 107° and 109° it exhibits signs of actual fusion. Towards 120° it gives off slightly acid water smelling like formic acid; towards 160° a few drops of acid liquid which reduce silver nitrate; and above 180° a small quantity of oily matter which solidifies to a white mass on cooling. When dissolved in glacial acetic acid and treated with bromine, it gives off hydrobromic acid, even when the liquid is cooled,

and does not yield any crystalline compound. This reaction indicates that it contains more hydrogen than santonin, that in fact it is a hydrosantonin, a view which is in accordance with its mode of formation. It has not, however, yet been obtained in a state fit for analysis. It forms non-crystalline compounds with alkalis and alkaline earths.

H. W.

The Isomeric α- and β-Derivatives of Naphthalene. By C. LIEBERMANN and A. DITTLER (Deut. Chem. Ges. Ber., vi, 945—951).

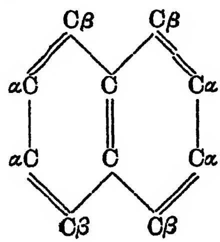
WHEN *α-nitracetonaphthalide*, $C_{10}H_6(NO_2)NH(CO.CH_3)$, is boiled with alcoholic potash, it is converted into *nitronaphthylamine*, $C_{10}H_6(NO_2)(NH_2)$; at the same time some nitronaphthol (together with ammonia) is formed, which remains in solution on precipitating the alcoholic alkaline solution with water.

Nitronaphthylamine crystallises from alcohol in long orange-yellow needles, melting at 191°. It is sparingly soluble in water, but freely in alcohol, and dyes wool intensely yellow, like picric acid. It dissolves more freely in hot nitric acid than in water, but crystallises out on cooling without forming a nitrate. It is isomeric with the nitronaphthylamine, melting at 118°—119°, which Beilstein and Kuhlberg obtained from dinitronaphthalene. With potassium dichromate it gives a green flaky precipitate, whilst the acetyl-compound is not changed by this reagent. By treating its concentrated alcoholic solution with nitrous acid, a compound is formed, separating from boiling xylene in reddish-violet crystals, consisting apparently of *nitramidodinaphthylimide*, $C_{20}H_{23}(NO_2)_2N_3$. When nitronaphthylamine is suspended in water, and nitrous acid is passed into the cold liquid, a large portion dissolves, and on boiling the filtrate with alcohol, *α-mononitronaphthalene* is obtained. The same compound is obtained from Beilstein and Kuhlberg's nitronaphthylamine.

Amidacetonaphthalide hydrochloride, $C_{10}H_6\begin{cases}NH(CO.CH_3)\\NH_2.CCH\end{cases}$, is readily obtained by reducing nitracetonaphthalide with tin and hydrochloric acid, and treating the solution with hydrogen sulphide. It forms long white needles. Its dilute solution gives with picric acid a precipitate crystallising from boiling water in yellow needles, $C_{10}H_6\begin{cases}NH(CO.CH_3)\\NH_2(C_6H_2(NO_2)_3OH\end{cases}$. Potassium dichromate produces in a concentrated solution a yellow precipitate crystallising from hot water in orange-coloured needles, and which at 100° have the composition $C_{10}H_6\begin{cases}NH(CO.CH_3)\\NH_2.Cr_2O_7H_2\end{cases}$. These salts are insoluble in strongly acid solutions. On boiling down the solution of the hydrochloride, a large portion is converted into diamidonaphthalene. This decomposition is more complete when an alkali is present. By adding hydrochloric acid to a solution of the base, the salt $C_{10}H_6(NH_2.ClH)_2$ is precipitated in silvery scales. The nitrate and sulphate are similar compounds. This diamidonaphthalene is isomeric with that which Hollemann obtained from dinitronaphthalene, but most probably identical with the

compound which Perkin prepared by acting with nascent hydrogen on azodinaphthyldiamine. The smallest quantity of this compound gives with a solution of potassium dichromate a green colour, and, when present in larger quantity, a green precipitate is formed and a strong smell of quinone given off. On boiling a dilute solution of the hydrochloride with a chromic acid solution containing 1 per cent., *naphthoquinone* distils over, identical with that obtained by Groves. When the quinone is boiled down with pure nitric acid, it is oxidised to *phthalic acid*, but only a trace of oxalic acid is formed.

The formation of phthalic acid shows that in the compounds here described the two side-chains are combined with the same aromatic nucleus. Further, it still appears most probable that the two oxygen-atoms of quinones are combined with two adjoining carbon-atoms. The side-chains would therefore both occupy the α position, as is seen from the following diagram :—



C. S.

Action of the Chlorides of Aromatic Acids on Aromatic Hydrocarbons. By V. Merz and Grucarevic (Deut. Chem. Ges. Ber., vi, 966).

α-Naphthyl-phenyl ketone is formed by acting on naphthalene with benzoyl chloride containing some benzoic acid and phosphorus chloride; at the same time a little β-naphthyl-phenyl ketone is produced.

When a mixture of naphthalene and α-naphthoyl chloride is heated with zinc, a ketone is formed, which is identical with that obtained from naphthalene and α-naphthoic acid. The same compound is also produced by the action of β-naphthoyl chloride on mercury-dinaphthyl, and must therefore be called α-β-dinaphthyl ketone.

β-naphthoyl chloride and naphthalene yield a mixture of two isomeric ketones, which may be separated by recrystallisation from a mixture of chloroform and ether. One crystallises in needles melting at 125°; the other forms plates which melt at 164°. The same mixture was obtained from β-naphthoic acid and naphthalene.

C. S.

Nitroanthracene and its Derivatives. By E. Schmidt (Deut. Chem. Ges. Ber., vi, 494).

The author has already shown that by reducing nitroanthracene with tin and hydrochloric acid, there is formed a hydrocarbon isomeric with

anthracene. The melting point of this product is 247°, but it is not identical with para-anthracene (melting at 244°). The new hydrocarbon can be repeatedly melted and heated to 300° without causing any alteration in its melting point, whereas para-anthracene is converted by fusion into ordinary anthracene of melting point 213°.

The picric acid compound of the new hydrocarbon is produced with less ease than that of ordinary anthracene, its formation being dependent on the strength of the solutions used. It forms fine red needles, often an inch in length, having the composition $C_{14}H_{10}.C_6H_2(NO_2)_3.OH$. Owing to the separation of uncombined hydrocarbon together with the crystalline picric acid compound, it is difficult to obtain pure.

Strong nitric acid boiled with the finely divided hydrocarbon converts it into a yellow nitro-product, $C_{14}H_9NO_2$, no trace of a quinone being formed. This nitro-product sublimes in yellow needles melting at 209°. It is only slightly soluble in alcohol, more readily in hot benzene. (Para-anthracene on nitration is partly unaltered, partly converted into ordinary anthracene, which yields anthraquinone and dinitro-anthraquinone.)

Bromine combines with the new hydrocarbon, forming a well-crystallised compound, $C_{28}H_{19}Br_3$, apparently formed by addition of Br_2, duplication, and elimination of HBr: this melts at 273°, without any formation of hydrobromic acid, sublimes unaltered, and is scarcely attacked by caustic potash.

By dissolving the hydrocarbon in glacial acetic acid, and adding chromic acid, a quinone, $C_{14}H_8O_2$, is produced. Unless the mixture be carefully cooled, the action is apt to go much further, carbon dioxide being evolved. This quinone crystallises in red needles, sublimes unaltered, melts at 235° (anthraquinone melts at 273°), and yields an unstable colourless hydroquinone by treatment with sulphurous acid. It dissolves in concentrated sulphuric acid, with a beautiful blue colour, which disappears on dilution, the unaltered quinone again separating. On heating it with soda-lime, hydrogen is evolved, and a body formed, the study of which is not completed.

Phipson has recently stated that nitroanthracene is obtainable by the direct action of nitric acid on anthracene. Both the nitrated body described by Phipson and its reduction-products differ from the substance investigated by the author, whose nitroanthracene was obtained by nitration in alcoholic solution. The amido-anthracene thence obtainable is a very weak base, not yielding crystalline compounds with acids. This substance is formed, simultaneously with the new hydrocarbon, by reducing the nitroanthracene with tin and hydrochloric acid. It does not yield a gold or platinum salt. With nitrite of potassium and hydrochloric acid a beautiful violet-blue tint is developed, which disappears on standing, nitrogen being evolved.

C. R. A. W.

Phthaleïn of Hydroquinone and Quinizarin. By F. GRIMM (Deut. Chem. Ges. Ber., vi, 506).

WHEN hydroquinone is heated to 130°—140° with strong sulphuric acid and phthalic anhydride, two bodies are produced, but in quantities much

smaller than those corresponding with the amount of material used. The first of these, the *phthalein of hydroquinone*, $C_{20}H_{12}O_5$, is colourless, and has a great resemblance to the phthaleïn of phenol; the yield of this is about 20—25 per cent. of the theoretical amount. It forms a crystalline alcoholate, $C_{20}H_{12}O_5.C_2H_6O$, which loses the alcohol of crystallisation at 100°—110°; it melts at 230°—234° (uncorrected) and decomposes at a higher temperature. From strong alcoholic solution the alcoholate crystallises out, but from dilute alcohol a hydrate, $C_{20}H_{12}O_5.H_2O$, the water of crystallisation of which is lost at 160°—180°. The formation of the phthaleïn is represented by the equation

$$C_8H_4O_3 + 2C_6H_6O_2 = 2H_2O + C_{20}H_{12}O_5;$$

it yields a crystalline acetyl derivative, $C_{20}H_{10}O_5(C_2H_3O)_2$, when heated with acetyl chloride.

The second compound, *quinizarin*, is isomeric with alizarin; the yield being only about 1 to 2 per cent. of the theoretical amount; its formation is indicated by the equation—

$$C_8H_4O_3 + C_6H_6O_2 = H_2O + C_{14}H_8O_4.$$

Quinizarin crystallises from alcohol in red needles, from ether in yellow plates; it melts at 194°—195° (uncorrected) after sublimation; at 192°—193° after crystallisation from alcohol. It perhaps bears to munjistin the same relation as alizarin to purpurin; with alkalis it gives a blue solution with a slight violet tint; with baryta, a beautiful blue-violet compound is produced; with alumina, a red lake with a violet shade; and with magnesia, a deep blue violet. The weakly alkaline solution becomes brown-red on the addition of ferric chloride, and gives a dark red precipitate with lead acetate.

Although quinizarin is only isomeric with alizarin, it gives rise to anthracene when heated with zinc-dust, the hydrocarbon produced melting at 210°—212°, yielding a red picric acid compound, and furnishing a substance resembling anthraquinone, and melting at 273° on treatment with glacial acetic acid and chromic acid.

The constitution of this substance is probably expressed by the equation—

$$C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}O + C_6H_4(OH)_2 = H_2O + C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}C_6H_2(OH)_2,$$

the phthalic anhydride first produced forming a di-hydroxyl derivative of anthraquinone, $C_6H_4\left\{\begin{matrix}CO\\CO\end{matrix}\right\}C_6H_4$: that of the phthaleïn simultaneously formed may be—

$$C_6H_4\left\{\begin{matrix}CO\ .\ C_6H_3\ .\ OH\\CO\ .\ C_6H_3\ .\ OH\end{matrix}\right\}O.$$

i.e., a derivative of phthalyl-ketone, $C_6H_4\left\{\begin{matrix}CO.C_6H_5\\CO.C_6H_5.\end{matrix}\right.$

Not improbably quinizarin may be found to be a constituent of artificial alizarin; it resembles alizarin in many points, and differs chiefly in the following respects. The former gives green-yellow

fluorescent solutions and characteristic absorption-bands, whilst the latter forms non-fluorescent solutions and gives different absorption-spectra. The author concludes his paper with a table of the differences between the spectra of alizarin and quinizarin when dissolved in caustic soda, potassium carbonate, ether, and sulphuric acid.

C. R. A. W.

Chrysin (Chrysinic Acid). By J. Piccard (Deut. Chem. Ges. Ber., vi, 884—889).

The author now finds that chrysin is present in the buds of *Populus monolifera* or *balsamifera*, and that these buds yield, under favourable circumstances, $\frac{1}{400}$ of their weight of pure chrysin. The method now adopted for the extraction of chrysin is as follows:—An alcoholic extract of 100 parts of the buds is precipitated by an alcoholic solution of 12 parts of lead acetate, and the next day the liquor is filtered from the precipitate, freed from lead by means of hydrosulphuric acid, and subjected to distillation in order to remove the spirit. The acid liquor remaining in the retort deposits a resinous mass, which is to be once crystallised from spirit, and then freed from fat, resin, sulphur, salicin, and populin, by successive treatment with absolute alcohol, ether, carbon sulphide, and boiling water. Boiling benzene now extracts from it a substance which the author calls *tectochrysin*. The impure substance is next fused at a temperature of 275°, in order to carbonize certain impurities, dissolved in alcohol, and treated with a few drops of basic lead acetate, freed from lead by means of hydrosulphuric acid, and finally crystallised twice from spirit.

Chrysin, when pure, forms bright yellow, thin, shining tables, which melt and sublime at 275°. It dissolves in about 50 parts of hot or 180 parts of cold alcohol. Acetic acid and aniline dissolve it with tolerable facility, ether less readily, and carbon disulphide, petroleum, benzene, or chloroform scarcely at all. It is insoluble in water, but aqueous alkalis dissolve it with a yellow colour, and if the solution has not been long boiled, unaltered chrysin is precipitated on the addition of an acid; but if the alkaline solution be boiled under an increased pressure, or if chrysin be heated with soda lime to 200°—300°, it becomes converted into an oily substance having an odour like that of bitter almond-oil. When an ammoniacal solution of chrysin is evaporated, unaltered chrysin remains, and the ammoniacal solution yields a yellow precipitate with calcium or barium chloride, and this becomes black when exposed, in a moist state, to the air. An alcoholic solution of chrysin is precipitated by lead acetate, but the precipitate is soluble in excess of the reagent or in acetic acid. Ferric chloride strikes a violet colour with an alcoholic solution of chrysin. Concentrated sulphuric acid and nitric acid dissolve it with a yellow colour, and the latter solution deposits granular crystals of nitrochrysin. The analysis of chrysin and its derivatives indicated $C_{15}H_{10}O_4$ as the formula of chrysin.

Dibromochrysin, $C_{15}H_8Br_2O_4$. This was obtained by mixing an alcoholic solution of chrysin with excess of bromine, and washing the slender needles which are deposited, with alcohol containing bromine.

When dried over sulphuric acid, it forms a felted mass of silky crystals which become exceedingly electric on pulverisation.

Di-iodochrysin, $C_{15}H_8I_2O_4$.—When iodine is added to an alcoholic solution of chrysin, the action is slow and incomplete, but the addition of iodic acid causes the action to take place rapidly, needles of di-iodochrysin being deposited. The same compound is formed when a solution of iodine in potassium iodide is added to an alkaline solution of chrysin. Di-iodochrysin is less stable than the bromine compound, as at 100° it loses weight and changes colour.

Chlorochrysin.—A derivative of chrysin was obtained inneedles when a solution of chrysin in acetic acid was subjected to theaction of a stream of chlorine.

Nitrochrysin.—A cold saturated solution of chrysin in strong nitric acid soon becomes warm, evolves nitrous fumes, and deposits a crystalline substance. The same body may be obtained by adding dilute nitric acid to chrysin, and evaporating off the acid. The product thus obtained is contaminated with oxalic acid, resinous substances, and the aromatic oily substances already referred to. It is purified by being first boiled with water and then with alcohol, after which the residue is dissolved in ammonia, and on evaporating this solution, crystals of *ammonium nitrochrysinate* are obtained. This salt can be easily purified by crystallisation, and it is then decomposed by an acid. Nitrochrysin is almost insoluble in alcohol, ether, benzene, &c., but dissolves in hot acetic acid or aniline, from which it may be obtained in large crystals. It forms two compounds with ammonia, an orange-red *basic salt* which is very slightly soluble, and is decomposed by being boiled with water, into ammonia and the *acid salt*. This latter has a bright yellow colour, and does not lose all its ammonia when water is repeatedly evaporated from it. A determination of the carbon and hydrogen in nitrochrysin led to the formula $C_{15}H_6(NO_2)_2O_4$.

The author regards chrysin as a homologue of alizarin and frangulic acid, and he hopes shortly to describe the action of alkalis and of zinc-dust on chrysin.

T. B.

Some Constituents of Poplar Buds. By J. Piccard (Deut. Chem. Ges. Ber., vi, 890—893).

Essential Oil of Poplar Buds.—One kilo. of the buds yielded 5—6 c.c. of an oil boiling at 260°—261° (cor.), and having a sp. gr. of 0·9002. Its composition corresponded with the formula, C_5H_8, and an old specimen was found to contain 3·48 per cent. of oxygen.

The boiling point of this oil appears to indicate that it is more condensed than oil of turpentine, but on oxidation the two oils behave alike.

When the acid liquor from which crude resinous chrysin has separated, is left to itself for some days, it deposits shining crystalline masses which apparently consist of a mixture of populin and salicin.

The crude chrysin was found to be contaminated with tectochrysin.

This substance is much more soluble in benzene than chrysin, and on this circumstance is founded the process for its separation.

Tectochrysin melts at 130°, does not dissolve in alcohol so readily as chrysin, and it separates from this solvent in long needles. It is deposited from benzene in yellow crystals belonging to the monoclinic system. Determinations were made of three combinations, and from these the inclination of the clinodiagonal to the principal axis was found to 53° 6′. The principal axis, clinodiagonal, and orthodiagonal were to one another as 1·54, 1, and 1·86. An analysis of tectochrysin led to the formula, $C_{16}H_{12}O_4$, while its bromine-compound gave numbers corresponding with the formula, $C_{17}H_{12}Br_2O_4$. The author is inclined to regard $C_{16}H_{12}O_4$ as the true formula of the substance. According to this view, it is the homologue standing next above chrysin.

T. B.

Action of Sodium Formate on Benzoic Acid.

By V. v. Richter (Deut. Chem. Ges. Ber., vi, 876—879).

Meyer has obtained isophthalic acid by fusing bromobenzoic acid or sulphobenzoic acid with sodium formate; and the author finds that when potassium benzoate is fused with sodium formate, both isophthalic acid and terephthalic acid are formed, the former being produced in a larger proportion than the latter. Oxalic acid is also formed, but this substance is produced when sodium formate is fused by itself.

The author considers it probable that when sulphobenzoic acid or bromobenzoic acid is fused with sodium formate, the hydrogen evolved by the decomposing formate first exercises a reducing action and gives rise to the reproduction of benzoic acid, this being afterwards acted on by a fresh portion of the formate.

T. B.

Acetyl Picrate.

By D. Tommasi and H. David (Compt. rend., lxxvii, 207—210).

When one part of picric acid and four parts of acetic anhydride are heated in a reflux-apparatus for two hours (temperature not given), a yellowish liquid is obtained, which consists of acetic anhydride holding in solution acetyl picrate, $\left.\begin{matrix}C_6H_2(NO_2)_3\\C_2H_3O\end{matrix}\right\}O$. On adding water, the new compound is precipitated as a yellowish-white crystalline powder, which is washed with water and dried, first by pressure and then *in vacuo*. Acetyl picrate melts at 75°—76°, becoming pale yellow and oily; at 120° it gives off acetic acid; at 180° it darkens, and at 260° it completely decomposes. It is soluble in ether, alcohol, and ethyl acetate, in sulphuric, nitric, and hydrochloric acids. A few hours' exposure to air, and even less when in contact with water, causes it to become yellow, owing to partial decomposition. With an alkali it splits up into picrate and acetate of the alkaline metal. The ethereal solution, when evaporated, deposits beautiful crystals of a deep yellow colour.

Acetyl picrate does not detonate when struck, unless potassium chlorate be mixed with it, in which case it explodes with violence.

B. J. G.

Action of Iodic Acid on Pyrogallic Acid. By JACQUEMIN (Compt. rend., lxxvii, 209—211).

A 5 per cent. solution of pyrogallic acid is not acted upon by concentrated nitric acid, by aqua-regia diluted with twice its volume of water, or by arsenic acid. Iodic acid, on the contrary, reacts immediately on a solution containing one part of pyrogallic acid in 250 of water. Bromic acid has no action on pyrogallic acid, and even chloric acid, which parts with its oxygen to iodine, requires to be in that state of concentration in which it attacks paper, before any reaction takes place. Pyrogallic and iodic acids are, therefore, excellent tests for each other. The latter may be detected in a solution containing $\frac{1}{100}$ milligram, and its amount accurately determined in a solution ten times stronger. The reaction results in the formation of a brown colour, and, after a time, of a precipitate, which appears to be the purpurogallin of Girard. The filtrate from this precipitate, when treated with sodium chloride, sometimes yields a brownish-black precipitate soluble in water, insoluble in alcohol, and presenting the characteristics of tannomelanic acid, which is probably formed thus:

$$3C_6H_6O_3 + HIO_3 = 3C_6H_4O_3 + 3H_2O + HI.$$

In other instances, a small precipitate only is produced by sodium chloride, which is soluble in both alcohol and water. The filtrate from this precipitate yields an abundant black precipitate with ammonia. (It is not stated under what conditions these different results are obtained.)

B. J. G.

Action of Phosphorus Pentachloride on Phenolparasulphonic Acid. By A. KEKULÉ (Deut. Chem. Ges. Ber., vi, 943—945).

WHEN potassium phenolparasulphonate is heated with phosphorus pentachloride and the product submitted to distillation, first thionyl chloride and phosphorus oxychloride pass over, and then a liquid from which, by fractional distillation, *chlorophenylphosphoric chloride*, $POCl_2(OC_6H_4Cl)$, can be isolated. This compound is formed by the action of phosphorus oxychloride on monochlorophenol, which is the first product of the reaction—

$$C_6H_4Cl.OH + POCl_3 = POCl_2(OC_6H_4Cl) + HCl.$$

Chlorophenylphosphoric chloride is an oily, very refractive liquid, boiling at 265° and possessing the pungent smell of the acid chlorides. It is very hygroscopic, and when exposed to the air is readily converted into the crystalline *chlorophenylphosphoric acid*, $PO(OH)_2(OC_6H_4Cl)$, which, however, cannot easily be obtained in the pure state, because water easily resolves it into phosphoric acid and common chlorophenol. This compound may be obtained in quantity by heating the chloride in sealed

tubes with water. The author formerly found that phenylparasulphonic acid is converted into resorcin by fusing it with potash, but he believes now that this is doubtful, because Petersen has found that hydroquinone is formed when common chlorophenol is fused with potash. Phosphorus pentachloride acts briskly on chlorophenylphosphoric acid, converting it partly into the corresponding chloride and partly into common dichlorobenzene. The latter compound is also contained in the portion of the original product boiling between 120° and 265°. It is partly produced by the action of the pentachloride on monochlorophenol and partly derived from chlorophenylphosphoric chloride, which, when heated with phosphorus pentachloride, is decomposed according to the following equation:—

$$POCl_2(OC_6H_4Cl) + PCl_5 = 2POCl_3 + C_6H_4Cl_2.$$

C. S.

Dibenzyldisulphonic Acid. By R. KADE (Deut. Chem. Ges. Ber., vi, 953—955).

THIS acid is produced by shaking fused dibenzyl with warm sulphuric acid; on cooling the liquid solidifies to a magma of crystals, forming, after draining, a light reddish white mass, which, on standing in the air or on addition of a little water, forms a solution from which, on standing, the hydrate, $C_{14}H_{12}(SO_3H)_2 + 5H_2O$, crystallises out in tufts of long needles, whilst by evaporating the solution *in vacuo* large plates are formed.

$C_{14}H_{12}(SO_3K)_2 + 2H_2O$ crystallises in silvery plates. On purifying the crude salt, a small quantity of reddish warty crystals were obtained, consisting of $C_{14}H_{10}(SO_3K)_4 + 3H_2O$.

$C_{14}H_{12}(SO_3)_2Ba + \frac{1}{2}H_2O$ and $C_{14}H_{12}(SO_3)_2Pb + H_2O$ are not insoluble in water, as Fittig and Stelling have stated; they separate from a boiling solution in warty masses.

By fusing the potassium salt with potash and adding hydrochloric acid to the solution of the melt, a precipitate was formed which, after crystallisation from acetic acid, was found to be *oxydibenzylsulphonic acid*, $C_{14}H_{12}\begin{cases}SO_3H\\OH\end{cases}$.

C. S.

Action of Alcoholates and Phenates on Amides. By W. WEITH (Deut. Chem. Ges. Ber., vi, 966).

WHEN oxamide is distilled with sodium ethylate or sodium or potassium phenate, the cyanides of these metals and ammonia are produced, but neither ethylamine nor aniline. Caustic potash and oxamide also yield a large quantity of potassium cyanide. Urea and sodium ethylate yield only ammonia, and acetanilide and sodium phenate give diphenyl, aniline, acetone, and a very small quantity of a crystalline solid having the properties of diphenylamine. A trace of the latter body is also produced by heating sulphocarbanilide with sodium phenate.

C. S.

Action of Potassium Sulphydrate on Aromatic Nitriles.
By A. WEDDIGE (J. pr. Chem. [2], vii, 99).

UNDER the supposition that potassium sulphydrate would act upon nitriles in an analogous manner to potassium hydrate, with formation of sulpho-acids corresponding to the oxygen acids, the author heated pure benzyl cyanide ($C_6H_5.CH_2CN$) with an excess of potassium sulphydrate dissolved in alcohol for several days on the water-bath.

The substance obtained proved to be the amide of alphatoluic acid $C_6H_5CH_2.CONH_2$ (phenyl-acetamide) instead of the expected potassium disulpho-alphatoluate, $C_6H_5.CH_2.CSSK$.

As the only account given of this amide is in a short notice by Strecker, the author states that its chief properties are that it dissolves very sparingly in cold water, and crystallises out from its solution in hot water in thin brilliant plates. It dissolves easily in alcohol in the cold, and from a hot saturated solution it may be obtained in beautiful crystals, often half an inch long, of an extraordinary mother-of-pearl brilliancy.

Ether dissolves it with difficulty. It melts at 154°—155°, and boils without decomposition between 181°—184°. By boiling this amide with an alcoholic solution of potash, an acid was obtained, having the exact melting point of alphatoluic acid, 76°—77°.

In the filtrate from the amide an acid containing sulphur was obtained by the addition of hydrochloric acid, but it requires further investigation.

Benzonitrile treated with potassium sulphydrate gave benzamide.

The investigation was not extended to the group of fatty acids.

G. T. A.

α-Cyanonaphthalene. By W. WEITH
(Deut. Chem. Ges. Ber., vi, 967).

THIS nitrile of α-naphthoic acid is produced by heating sulphocarbonaphthalide with finely divided copper; at the same time, some naphthylamine is formed.

C. S.

Preparation of Aromatic Sulphur-Ureas. By W. WEITH
(Deut. Chem. Ges. Ber., vi, 967).

THESE compounds are readily formed by heating an alcoholic solution of aniline or other amido-compounds with one molecule of caustic potash and an excess of carbon sulphide for one hour. On adding dilute hydrochloric acid to the product and boiling off the alcohol, the sulphur-urea crystallises out and can be easily purified by one recrystallisation. Aniline yielded 80 per cent. of pure sulphocarbanilide.

C. S.

Decomposition of Rosaniline by Water. By C. LIEBERMANN
(Deut. Chem. Ges. Ber., vi, 951—953).

WHEN rosaniline is heated with water in a copper digester to 270°, a large quantity of phenol is formed, which is got rid of by boiling the

product with steam. The residue contains carbonaceous matter and a compound containing no nitrogen, together with nitrogenous bodies. They are removed by boiling with water, and heating the crystals which separate out from the filtrate with crude hydrochloric acid, which dissolves only the nitrogen-compounds. The residue crystallises from boiling water in pointed plates melting at 200°, and from alcohol in small plates. It dissolves in alkalis without colour, and with sodium-amalgam and water it gives a red solution which soon becomes colourless. This compound contains C = 72·5; 72·6; 73·3; 73·4; and H = 5·0; 5·3; 5·9, or less than required for the formula $C_{20}H_{16}O_3$ + H_2O; it does not change its composition at 170°. It has nothing in common with rosolic acid or with hydrorosolic acid. By heating it with hydriodic acid to 160°, or with hydrochloric acid to 200°, it is resolved into phenol and cresol. Acetic anhydride converts it at 160° into a compound crystallising from alcohol in needles melting at 156°, and containing C = 68·25 and H = 5·21. Heated with phosphorus pentachloride containing some trichloride to 170°, it yields $C_{20}H_{15}Cl_3O_2$, crystallising from alcohol in colourless plates melting at 137°. This compound is not changed by heating it with alcoholic potash, and by boiling it with sodium-amalgam only a part of the chlorine is removed.

C. S.

Methyl-aniline Green. By H. Appenzeller (Deut. Chem. Ges. Ber., vi, 965).

Binscheider and Busch in Bâle, manufacture an aniline green occurring in commerce in splendid crystals, which are readily soluble in water and distinguished by their purity and richness of colour. This compound consists of $C_{20}H_{16}(CH_3)_5Cl_2N_3.H_2O$ + $ZnCl_2$, being a double salt of zinc chloride and an aniline green differing from Hofmann's and Girard's iodine-green by containing chlorine in place of iodine. By treating it with silver nitrate it is converted into the nitrate, which possesses very similar properties. In acids it dissolves with a yellowish-brown colour, which is reconverted into the original green by adding a large quantity of water. The water contained in the crystals is given off only when the compound is left *in vacuo* for a long time, and therefore the constitution of the green is explained by the following formula:—

$$C_6H_4\left\langle\begin{matrix} N(CH_3)_2Cl-C_7H_6 \\ N(CH_3)_2Cl-C_7H_6 \end{matrix}\right\rangle NH(CH_3)OH.$$

C. S.

Physiological Chemistry.

A New Constituent of Urine. By T. Baumstark (Deut. Chem. Ges. Ber., vi, 883—884).

Urine was evaporated on the water-bath to a syrup, and this was mixed with a considerable quantity of absolute alcohol. The alcoholic

filtrate was freed from spirit by distillation, and the residue, after the removal of hippuric acid by ether, was neutralised with ammonia, treated with basic lead acetate, and filtered. On evaporating this filtrate, crystals of urea were obtained, together with crystals which did not dissolve in spirit. These crystals are slightly soluble in cold water or aqueous alcohol, moderately soluble in hot water, insoluble in absolute alcohol or ether. Analysis of the new substance led to the formula, $C_3H_8N_2O$. It forms white prisms resembling hippuric acid and melting above 250°. When strongly heated, it is decomposed, with production of white fumes having a peculiar odour, and a combustible gas which smells like ethylamine and has an alkaline reaction. The new substance forms easily soluble salts with acids, and although it does not combine with bases, its solution is precipitated by mercuric nitrate. Nitric acid converts it into sarcolactic acid, and boiling with baryta-water causes the separation of half the nitrogen in the form of ammonia; the other half is apparently separated as ethylamine, barium carbonate being deposited. These reactions may be explained by representing the formula of the new body as follows: $NH_2—CO—C_2H_4NH_2$, and the action of alkalis on it may be represented by the following equations:—

(1) $NaHO + NH_2.CO.C_2H_4.NH_2 = NH_3 + NaCO_2.C_2H_4.NH_2$.
(2) $NaCO_2.C_2H_4.NH_2.NaHO = Na_2CO_3 + C_2H_5.NH_2$.

T. B.

The Cartilage of the Shark. By P. PETERSEN and F. SOXHLET (J. pr. Chem. [2], vii, 179—181).

THE cartilage of a fresh specimen of *Scymnus borealis* formed an elastic mass which was almost transparent when in thin sections, and on drying became covered with crystals of sodium chloride.

Analysis showed it to consist of—

Organic matter resembling chondrin, and containing 15·4 per cent. of nitrogen	8·03
Inorganic matter	17·77
Water	74·20
	100·00

The inorganic matter contained—

Common salt	94·24
Soda	0·79
Potash	1·64
Lime	0·40
Magnesia	0·05
Iron oxide	0·27
Phosphoric acid	1·03
Sulphuric acid	1·88
	100·30

These figures correspond with 16·69 per cent. of common salt in the

fresh substance, and 4·80 per cent. of nitrogen in the dried cartilage. As the fresh fish contains only 1·16 per cent. of inorganic matter, it becomes a subject of interest to inquire whether so great an accumulation of salt in the cartilage is due to chemical combination, or to some kind of osmotic attraction exercised by the substance of the cartilage.

T. B.

Brittleness of the Bones in Cattle. By J. Nessler (Landw. Versuchs-stationen, xvi, 187—192).

A disease in cattle occurs nearly every year in some parts of the Black Forest, during which the bones of the affected animals become very brittle. It most frequently attacks cows in calf and young cattle, and occurs only on particular farms which overlie granite or sandstone; the contiguous farms on which the disease never appears, or only in very dry seasons, are mostly on gneiss. The animals are often cured by change of pasturage. Analysis of various bones of different sound and diseased animals gave the following results:—

Percentage of Dry Matter.

	Pelvis.		Vertebræ.		Forearm.		Tibia.		Joint of tibia.		Os Femoris.
	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Diseased.
Ash	45·49	36·75	45·50	28·09	64·27	65·96	61·02	66·95	34·82	24·41	63·30
Phosphoric acid	15·93	12·81	18 81	10·59	27·68	29·22	25·92	25·74	14·08	9·36	23·96
Lime	—	18·54	—	—	36·15	35·71	32·81	—	18·21	12·71	35·60
Fat	25 52	36·65	22·65	36·00	1·63	3·96	1·90	1 57	26 70	58·61	2·14
Nitrogen	3·77	4·00	3·41	4·76	4·09	3·84	4·62	4·72	4·15	—	4·47

Percentage of Ash.

	Pelvis.		Vertebræ.		Forearm.		Tibia.		Joint of tibia.		Os Femoris.
	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Sound	Diseased.	Diseased.
Phosphoric acid	35 02	34·88	41·34	37·69	43·08	44·29	43·92	38·45	42·89	38·33	37·86
Tricalcic phosphate calculated from ditto	76·34	77·04	90·24	82·16	94·04	96·68	95·86	83·91	93·63	83·67	82·63
Total lime	—	50 45	—	—	55·80	54·13	55·59	—	55·18	52·06	56·25
Lime not combined with phosphoric acid	—	9·19	—	—	4·90	1·74	3·63	—	4·74	6·72	11·47
Magnesia	—	·76	—	—	—	—	—	—	—	—	1·24
Potash	—	1·52	—	—	·29	·27	·20	—	·33	·41	·25
Soda	—	1·64	—	—	1·01	1·12	1·22	—	1·31	2·69	·30

Of the hollow bones only the walls were taken for analysis, without the joints or marrow. It is seen that in the spongy bones there is more fat and less ash and phosphoric acid in the diseased specimens than in the sound; in the long bones no such difference is seen. With the exception of the bones of the forearm, there is a smaller percentage of phosphoric acid in the ash of the diseased bones.

The bones of diseased animals appear to be less in weight than the bones of a healthy animal of the same size. In many cases the disease is in all probability due to an insufficiency of lime and phosphoric acid in the food.

E. K.

Estimation of Hæmoglobin in Blood. By M. QUINQUAUD (Compt. rend., lxxvi, 1489).

THE author finds that there is an exact relation between the quantity of oxygen which blood can absorb and the amount of hæmoglobin it contains, so that the latter can be determined by ascertaining the former. The quantity of oxygen absorbed by 100 cubic centimeters of human blood is 260 c.c., of ox-blood 240 c.c., and of duck's blood 170 c.c. The quantities of iron in 1000 grams of these kinds of blood are 0·53, 0·48, and 0.34 grm. respectively. According to Hoppe-Seyler's computation, that 0·43 grm. of iron corresponds with 100 grams of hæmoglobin, the quantities of this substance in 1000 grams of these kinds of blood are 125, 120, and 82 grams respectively. The numbers obtained by Preyer from observations with the spectroscope are a little higher, but bear the same proportions. The amount of hæmoglobin in the blood of the fowl is nearly the same as in that of the duck.

T. L. B.

Variations in Hæmoglobin in the Zoological Series. By QUINQUAUD (Compt. rend., lxxvii, 487—489).

BY the method of estimating the amount of hæmoglobin, depending on the action of a hyposulphite, the author has been enabled to draw up a table showing the variations in the weight of hæmoglobin contained in the blood in various animals and under different physiological conditions.

His researches lead him to the following results:—

1st. The progressive diminution in the amount of hæmoglobin contained in equal volumes of the blood follows, as a rule, the steps of the animal scale.

2ndly. The blood of young animals contains less hæmoglobin than that of adults. A line representing the amount of hæmoglobin takes the following course. It falls slightly during the first few days of extra-uterine life, rises during childhood, remains horizontal during adult life, and finally falls slowly during old age.

3rdly. The blood of birds is much less rich in hæmoglobin than that of mammals, but the weight of the globules is rather greater in the former than in the latter, though the mammalian globules contain only a third of the quantity of albuminous material present in those of birds.

4thly. As a rule, the females have less hæmoglobin than the males.

5thly. The lymph of crustaceans contains 4 to 5 cubic centimeters of oxygen in 100, whereas ordinary water in the middle of winter, when completely saturated, contains only 1 cubic centimeter in 100.

E. C. B.

The Saccharifying Ferment of the Blood. By P. PLOSZ and E. TIEGEL (Pflüger's Archiv für Physiologie, vii, 391—398).

THE authors investigate the nature of the saccharifying action which the blood shows at the moment in which its blood-cells become dis-

solved, described by Tiegel in his treatise "On the fermentation of the blood" (*Pflüger's Archiv f. Phys.*, vi, p. 249).

Experiment.—10—12 volumes of $\frac{1}{2}$—$\frac{3}{4}$ p.c. NaCl solution are added to a suitable quantity of whipped blood. The mixture is poured into a shallow vessel and left for 24 hours at a temperature below 50°. By this time the blood-cells have settled to the bottom, sharply separated from the liquid above, which the authors name the "wash-liquid." Albumin is separated from the liquid by coagulation. If, after a time, traces of sugar or considerable quantities of peptone are found in the liquid, it is considered unfit for experiment. If this be not the case, the following experiments are made with it:—

(i.) 25 c.c. of the "wash-liquid" are mixed with starch and digested in the hatch-oven for an hour, then tested for sugar; it is found in greater or less quantity.

(ii.) 25 c.c. of the liquid, rich in blood-cells, are removed from the bottom of the vessel and mixed with starch paste until it becomes lac coloured. If, after an hour, saccharification has taken place, the wash-liquid is separated as well as possible, and replaced by a similar quantity of NaCl-solution cooled to 5°. After 24 hours the fermentation will have disappeared entirely or will be perceptible only after a longer time, or after adding more of the liquid containing blood-cells.

(iii.) The rest of the blood-cells, together with the supernatant wash-liquid, are allowed to stand at 20°—30° for 24 hours. Gradually the blood-cells dissolve and impart colour to the liquid. It may be shown by testing that a destruction of the ferment takes place, proportional to the solution of the blood cells, and is complete at the end of 24 hours.

The above phenomena are thus explained. According to Expts. i and ii, together with i and ii given in Tiegel's treatise (quoted above), a ferment exists in the blood, which is generally so combined that it is hindered from acting. By the treatment described above, the combination is dissolved, and the ferment sets to work. Possibly the ferment exists in combination with a globulin substance; for by the action of a solution of sodium chloride, a globulin substance which contained a saccharifying ferment was extracted from fibrin, after the fibrin had been thoroughly washed with water. It may be that the ferment of the blood is combined in the blood-cells, and that this combination is dissolved in a similar manner. Whether the cause which brings about the solution of the blood-cells is the same as that which destroys the ferment, cannot at present be determined.

The destruction appears to set to work in full measure only after solution of the cells, as shown in the following experiments: 3 c.c. of active pancreas-glycerin are mixed with 15 c.c. of washed blood-cells, digested for 24 hours at a temperature below 5°, then for one hour with NaCl-paste in the oven: saccharification has clearly taken place. The rest of the mixture is digested for 24 hours: saccharification still evident. The blood-cells are dissolved with ether, and the mixture again digested for 24 hours: saccharification is quite destroyed.

Moreover, a saccharification artificially set up in starch and albumin is destroyed by addition of the blood-cell solution. In order to see whether a ferment is combined in blood-cells of living-blood in a

similar way, Bock and Hoffmann's experiments were repeated, and with success. The authors explain the results by supposing that the solution of sodium chloride washes out ferment from the blood and glycogen from the liver. A ferment was obtained from the urine of an animal experimented on, and also from human diabetic urine; Béchamp has obtained a similar ferment from normal urine. The authors conclude that the fermentation takes place not in the kidneys or urine, but in the liver or blood, but contend against von Wittich's supposition that the saccharification in the liver is caused by a ferment contained in the liver-cells.

C. O.

The Blood in Apnœa. By AUGUST EWALD (Pflüger's Archiv f. Physiologie, vii, 575—581).

MAINLY of interest to the physiologist. The author finds that in apnœa, produced by inflating the lungs with a pair of bellows, the quantity of oxygen in arterial blood is increased until this becomes almost saturated, whilst the amount of oxygen in the venous blood is diminished. He also states that it appears from some unpublished experiments of Pflüger's, that in apnœa the consumption of oxygen is neither increased above, nor diminished below, the normal.

T. S.

The Part played by Gases in the Coagulation of Albumin. By E. MATHIEU and V. URBAIN (Compt. rend., lxxvii, 706—709).

PROCEEDING from the observations that the serum of blood, when deprived of its gases is not coagulable by heat, even at a temperature of 100°, and that egg-albumin exhibits the same anomaly, the authors have investigated the causes of the coagulation of albumin, and the relations of this substance to globulin. They state that the pneumatic mercury pump enables them to deprive albumin not only of gases, but also of volatile salts. Deprivation of gases renders albumin incoagulable by heat; and the disappearance of volatile salts converts it into a substance analogous to globulin. They find that—

1. Carbonic acid is the agent which determines the coagulation of albumin by heat. Egg-albumin, which abounds in carbonic acid, is not coagulable at a temperature of 100° when deprived of this gas, but is still precipitable by alcohol acids and metallic salts. Re-addition of carbonic acid renders the albumin again coagulable by heat alone. Albumin coagulated by heat contains carbonic acid and gives it up when treated with acids *in vacuo*.

2. Albumin when deprived of its volatile salts is converted in globulin. These volatile salts consist of ammonium carbonate, with traces of the sulphate and sulphide. The addition of a trace of ammonium carbonate to a solution of globulin, converts it into albumin. The solution is no longer coagulable by carbonic acid in the cold, but coagulates at a temperature of 70°.

A solution of globulin treated with 1–200th of an alkaline phosphate, acquires the properties of casein, and is coagulated by acetic acid. If, on the other hand, albumin, casein, and fibrin be dissolved by the aid of ammonia, and submitted to evaporation at ordinary temperatures, a substance is produced which appears to be globulin. From these facts the authors conclude that globulin is comparable with Mulder's protein, in that it is a substance from which all other albuminoids are derived.

T. S.

Variations in the amount of Urea excreted under the Influence of Caffeine, Coffee, and Tea. By L. RABUTEAU (Compt. rend., lxxvii, 489—491).

THIS paper, as the author states, was called forth by a previous one by M. Roux, on the same subject. Roux's results were at variance with those of the author, inasmuch as they showed that tea and coffee increased the amount of urea.

The author describes two sets of experiments, one made by Eustriades, of Smyrna, and the other by himself.

In the experiments of Eustriades, which were made on his own person, 15 centigrams of caffeine produced a diminution in the urea of 11 p. c., and 30 centigrams of the same diminished it by 28·2 p. c. Slowness of the circulation was also noticed. In another experiment, 60 grams of roasted coffee, taken in infusion, diminished the urea by 15·18 p. c., the circulation also being retarded.

Here the author remarks that in every case where a hot liquid, or even hot "eau sucrée" is taken, the circulation undergoes a temporary acceleration, which may possibly lead to errors.

The author's own experiments were made on himself, and the average results obtained are seen in the following table:—

	Urine in 24 hours.	Urea in 24 hours.	Pulse.
First Period. Ordinary Diet.			
April 4th to April 9th, 1870	1126 gr.	24·98 gr.	74
Second Period. 15 grams of Tea daily.			
April 9th to April 14th	1145 gr.	23·64 gr.	64
Third Period. Ordinary Diet.			
April 14th to April 19th..........	1046 gr.	25·00 gr.	68
Fourth Period. 15 grams of Green Coffee.			
April 19th to April 24th..........	1259 gr.	21·8 gr.	62
Fifth Period. Ordinary Diet.			
April 24th to April 29th..........	1242 gr.	26·18 gr.	69

Hence in the author's case, 15 grams of tea diminished the urea by

6·85 p. c., whereas the same quantity of green coffee diminished it by 14·11 p. c.

The fact of the augmentation in the urea in Roux's experiments being only transient, leads the author to expect that Roux will, in future experiments, arrive at results similar to his own. He proposes to make further experiments on this subject, in which he intends estimating not only the urea, but also the carbonic acid.

E. C. B.

Determination of the Mechanical Co-efficient of Aliments. By A. SAUSEN (Compt. rend., lxxvi, 1490—1493).

FROM data furnished by the General Omnibus Company of Paris, and also from those contained in General Morin's "Aide-Mémoire de Mécanique," the author concludes that in round numbers 1,600,000 kilogrammeters are the equivalent or practical co-efficient of 1 kilogram of protein, in a well-regulated diet. The omnibus horses of Paris weigh on an average 500 kilograms. Each one draws an average weight of 1,590 kilograms, at the rate of 2·20 meters per second, for four hours daily, and starts this weight 60 or 70 times. It thus performs daily work equal in round numbers to 2,000,000 kilogrammeters. At the rate of 1,600 per gram of alimentary protein, it would require 1,250 grams for its daily ration. It actually receives 1,402 grams, 960 of which are furnished by oats, 135 by bran, and 307 by hay. The difference of 152 grams goes to support the body supposed to be at rest at the rate of 30 grams per kilogram of weight, the quantity shown by experience to be necessary. The same co-efficient holds for the post-horses. They draw on an average 1,300 kilograms each, at the same rate as the omnibus horses, and receive 400 grams of oats for every kilometer traversed.

When the quantity of food necessary for the performance of internal physiological work, or, in other words, for the support of the body at rest, has been ascertained, the additional amount required for the performance of external work in ploughing, &c., may be calculated by the formula, $P = \frac{W}{C}$, P standing for alimentary protein, W for the work, and C for the mechanical co-efficient of the nutritive unit. To determine the work which may be obtained from a given quantity of food, the equation is $W = P \times C$. To express the ratio of food to work, in terms of oats, for example, one would have $\frac{P}{120} = \frac{W}{C}$, the kilogram of oats containing on an average 120 grams of alimentary protein, and *vice versâ*, if we designate by *n* the number of kilograms of oats. $N + 120 \times 1600$, will give the value of W.

T. L. B.

Influence of Barometric Pressure on the Phenomena of Life. By PAUL BERT (Compt. rend., lxxvi, pp. 1276—1280).

M. BERT finds the following phenomena in cases of death from poisoning by carbonic acid without want of oxygen, as in animals which repeatedly

respire a limited quantity of super-oxygenated air, or of compressed air. 1. The arterial blood remains rich in oxygen till death occurs, and at this moment it still contains 10 to 12 volumes of oxygen in 100 volumes of blood. The carbonic acid accumulates with decreasing rapidity, and a few seconds before respiration ceases, it attains the proportion of 110 to 120 volumes, or almost complete saturation, which seems to take place at 130 to 140 volumes. 2. The respirations become slower and slower, without proportionally increasing in amplitude, and at last they sometimes occur only every two or three minutes. 3. The pulls falls still more rapidly, but the heart continues to beat for several minutes after respiration has ceased. The arterial tension remains high throughout. 4. The temperature decreases with extraordinary rapidity, although oxygen is being absorbed. This shows that the oxidation processes which furnish heat diminish as the blood and tissues become saturated with carbonic acid, despite the entrance of much oxygen into the blood. At death the temperature is only 24° to 28° in the rectum, that of the surrounding medium being 15° to 18°. 5. When the carbonic acid in the arterial blood reaches about 80 volumes, all parts of the animal become completely insensible, with the exception of the eye, which does so only when the carbonic acid reaches 100 volumes. The animal remains perfectly quiet, without the least convulsion during the whole experiment. It is even difficult to say when death occurs. Convulsions occurring in suffocation, after hæmorrhage, or from ligature of the cerebral vessels, are due to deprivation of the nerve centres of oxygen, and not to the presence of carbonic acid. 6. After death, the motor nerves and muscles retain their properties as usual. 7. The tissues are charged with carbonic acid. The muscles contain 60 volumes of it, instead of 15 to 20, and it may reach 100 in the urine.

M. Bert draws particular attention to the fact that sensibility is destroyed long before the heart is affected, and thinks that carbonic acid deserves trial as an anæsthetic.

T. L. B.

Chemistry of Vegetable Physiology and Agriculture.

Influence of Changes in Barometric Pressure on the Phenomena of Vegetable Life. By Paul Bert (Compt. rend., lxvi, 1493—1497).

M. Bert has now extended his researches to vegetable life, and finds that changes in atmospheric pressure exercise upon it a similar action, to that which they have upon animal life, rarefied air being injurious on account of deficiency in oxygen, while compressed air, from its containing too much oxygen, has a positively poisonous action.

The present experiments were made on the germination of seeds, two kinds being employed, the one sort consisting of barley and oats in which the embryo, is accompanied by a starchy albumen, and the other of cresses and radishes in which an albumen is absent. In rarefied air germination begins with a rapidity corresponding to the smallness

of the pressure. The difference becomes evident from 50 centimeters. The number of seeds which succeed in germinating diminishes greatly. The lowest limit of germination is about 12 centimeters for cresses and 6 for barley. At these pressures the number of seeds which germinate is very small, and below them germination does not take place. The seeds which do not germinate are not dead, but germinate readily when the normal pressure is restored. The non-germination at low pressures is due to want of oxygen. At normal pressures, germination occurs more slowly when the air is poor in oxygen. It takes place as quickly as usual when the pressure is low, if the proportion of oxygen in the air is increased. It occurs as low as 4 centimeters in pure oxygen. The inferior limit of oxygen in air at which germination will occur as found by Hubert and Senebier, corresponds very closely with that just indicated for atmospheric pressure. The germination of lettuce-seeds ceased when the oxygen of the air was reduced to $\frac{1}{7}$th. Now, $\frac{1}{7}$th of 76 centimeters is 11 centimeters, the normal tension for cress-seeds.

In experiments with compressed air, a distinction must be drawn between those made in closed vessels and those in which the air has been frequently renewed, as in the former sort the influence of carbonic acid is to be considered as well as that of the compressed air itself. In fact, neither cresses nor barley, nor even the mould which grows on moist grain, will germinate in air containing 20 per cent. of carbonic acid, although an abundance of oxygen is at the same time present. This proportion of carbonic acid does not kill the seeds, but when it reaches 75 per cent., their vitality is destroyed, and they do not germinate when sown in the open air afterwards. The toxic power of carbonic acid both over animals and plants, is measured by its tension, so that the proportion which arrests germination is 10 per cent., and at 10 atmospheres it is 2 per cent. The toxic tension of carbonic acid is much the same for animals and vegetables. Compressed air, when kept pure by renewal, has no particular effect, or even seems beneficial, until the pressure reaches 4 or 5 atmospheres. Above this it is injurious, especially to seeds having a starchy albumin. At high pressures, seeds are killed by exposure to the action of compressed air, either before or after germination has begun. This effect is due entirely to the high tension of the oxygen. The effect is much greater upon farinaceous seeds than upon others. Seeds sown in compressed air consume much less oxygen than those in air at the normal pressure. Excessive tension of oxygen, therefore, lessens oxygenation in plants, and it does so likewise in animals.

T. L. B.

Endosmose of Gases through Vegetable Membranes.

By A. Barthélemy (Compt. rend., lxxvii, 427—429).

The membrane employed by the author was the leaf of the begonia, which, by gradual withering during winter, had become reduced to mere cuticular tissue. When common air was dialysed through such a membrane, the gas passing through contained 31—41 per cent. of oxygen. The comparative permeability of the membrane to various gases was ascertained by exposing one surface of the membrane to the

gas, and relieving the other side of pressure, the experiments being continued till equal volumes of gas had in every case passed, the different times required showing the relative permeability. It appears that the leaf membrane admits carbonic acid 13 to 15 times more readily than nitrogen, and 5 to 7 times more readily than oxygen. This high relative permeability of carbonic acid is somewhat diminished if the gas be quite dry. These results are similar to those obtained by Graham with a caoutchouc membrane. The bearing of these facts on the absorption of carbonic acid by the leaves of plants is obvious.

R. W.

Respiration of Aquatic Plants. By P. SCHÜTZENBERGER and E. QUINQUAUD (Comp. rend., lxxvii, 272—275).

By adopting the speedy method of determining dissolved oxygen which titration with a hyposulphite affords, the authors have been able to make a multitude of experiments on this subject. Beer-yeast does not evolve oxygen under any circumstances; its absorption of oxygen from the surrounding water is unaffected by light or darkness, but greatly dependent on temperature. Below 10° scarcely any absorption takes place; at about 35° the absorption reaches its maximum, which is maintained up to 50°; at 60° the absorptive power is destroyed. Ten grams of yeast containing 26 per cent. of dry matter absorbed at 9° 1·4 c.c. of oxygen, and at 50° 24 c.c. of oxygen per hour. Ten grams of a very fine and fresh yeast-plant, containing 30 per cent. of dry matter, absorbed at 36° as much as 107 c.c. of oxygen per hour. The quantity of oxygen in the water does not affect the rapidity of the absorption until it falls below 1 c.c. per litre, absorption then continues more slowly till the water is entirely deprived of oxygen.

With chlorophyll plants, there is an absorption of oxygen which is always taking place, and also an evolution of oxygen in sunlight. With *Elodea canadensis*, evolution of oxygen ceases between 45° and 50°; at this temperature absorption of oxygen can be ascertained to occur equally in light or darkness. The absorption of oxygen is much less than in the case of yeast, but its relation to temperature is the same. Ten grams of *Elodea canadensis* absorb at 24° 1·2—1·8 c.c. of oxygen, and at 40° 4—4·5 c.c. of oxygen per hour. As before, the quantity of oxygen present has little effect on the result. By taking care that the water never became saturated with oxygen, the authors were able to use the same method for ascertaining the rate at which oxygen is evolved in sunlight. Ten grams of *Elodea canadensis*, evolved in various mixtures of pure water, and water saturated with carbonic acid, the following cubic centimeters of oxygen; the experiments lasted fifteen minutes, but are calculated for one hour.

Pure water.	Water saturated with CO_2.	Oxygen evolved.	Pure water.	Water saturated with CO_2.	Oxygen evolved.
Alone.	—	1·0	100	20—30	13·0
100	2·5	13·2	100	40	10·0
100	5—10	20·0	—	Alone.	3·0

When the evolution of oxygen from the plant is vigorous, and continued for an hour or two, the water becomes supersaturated with the gas, containing at 35° as much as 20 c.c. per litre; this oxygen is retained by the water for a long time.

R. W.

Ash of the Wood of Differently Manured Vines.

By J. Nessler (Landw. Versuchs-Stat., xvi, 185—187).

The vines were manured, as under, in the spring of 1869, and the branches cut off in February 1870, and analysed with the following results:—

Percentage of Dry Substance.

Manure.	Ash.		Nitrogen.	
	Nodes.	Internodes.	Nodes	Internodes.
Unmanured	3·38	2·89	·62	·60
Gypsum	3·69	2·80	·79	72
Potassium sulphate	3 32	2 62	·75	·62
Potassium chloride	4·33	2·90	95	·91
Potassium chloride, superphosphate, and ammonium sulphate	2 89	2·51	72	·11

Percentage of Ash.

Manure.	Phosphoric anhydride.		Potash.		Lime.	
	Nodes	Internodes.	Nodes.	Internodes.	Nodes.	Internodes.
Unmanured	9·15	9·02	16·98	16·76	30·16	25·66
Gypsum	8·43	8 99	17 20	20 72	23·29	21·92
Potassium sulphate	7 76	7·31	22 99	23 25	26·25	23·99
Potassium chloride	9 85	10·48	22 30	24·45	23·68	20·10
Potassium chloride, superphosphate, and ammonium sulphate	12·06	12 02	22 89	24 58	30 99	30·17

The vine, manured with potassium chloride, was especially rich in ash; while the percentage of ash in the vine manured with the mixture was very small, but this plant showed a larger growth of wood. The nodes in all cases were richer than the internodes in ash and in nitrogen, and with the exception of the plant manured with gypsum, their ash contained a larger percentage of phosphoric acid.

H. K.

Experiments on the Cultivation of Sugar-beet in the Campagna Romana. By F. SESTINI and G. DEL TORRE (*Gazzetta chemica italiana*, iii, 190—195).

THE experiments were made at Grotta Rossa, near Rome, on a piece of land divided into six equal portions, three of which were manured respectively with superphosphate, common ashes (? wood ashes), and stable manure, while a fourth was left unmanured. In these four plots the seed was sown in March, the fifth being left for transplanting the beets, and the sixth for later sowing.

The following table exhibits the mean weight of the roots, and the richness of the juice of plants gathered on the 1st of August, from the manured and unmanured plots:—

Varieties of Beet.	Average weight of the roots.		Sugar in 100 grams of juice.	
	Plants manured with superphosphate.	Unmanured.	Plants manured with superphosphate.	Unmanured.
	grams.	grams.	grams.	grams.
Vilmorin	706·33	430·00	11·075	10·995
Magdeburg	601·33	416·00	11·695	11·181
Silesian	749 00	411·00	8·023	10·912
Imperial	1339·33	415·00	11·401	8·703
Disette d'Allemagne .	818·00	307·66	11 381	13 026

The authors found that, next to superphosphate, ashes are the best manure for beet, on account of the potash salts which they contain. The results of transplanting were not satisfactory, except in the case of the variety called Disette d'Allemagne.

From experiments by Montanaro cited in the authors' original paper, it appears that manuring with castor-oil cake increases the quantity of sugar in the juice by about 1 per cent.

In plants harvested early in September, the weight of the roots was greater, but the proportion of sugar in the juice was rather less, the average proportion in all the varieties being 9·4 per cent. The largest roots were obtained from the plots manured with superphosphate and with stable manure. Roots weighing less than a kilogram yielded a juice richer in sugar than those of greater weight. From this it appears that there is an advantage in thick sowing, for, though the roots will then be smaller, a given weight of them will contain more sugar.

Plants gathered in October exhibited a slight diminution of weight in the roots, and a greater diminution in the proportion of sugar in the juice, a result doubtless due to the previous rains.

Lastly, the authors give a table of the total weight of the roots grown on each plot, reduced to a hectare of surface. The results show

that the greatest number of plants is obtained with thick sowing, and the smallest number on the plots manured with superphosphate, the total weight of the roots being, however, nearly the same in the two cases, and the proportion of sugar greatest in the plants which had been thickly sown.

In the following table no account is taken of the yield of the plots bearing transplanted beets, as it was very small:—

Sugar contained in the entire harvest of the beets :

Unmanured	2143 kilos.
Manured with ashes............	—
„ „ stable manure	2567 „
„ „ superphosphate ..	2939 „
„ „ stable manure	2950 „
(thick sowing) ..	3529 „

H. W.

Effect of Potassium Salts on the Growth of Potatoes.

By C. D. Hunter (Trans. Highland Agri. Soc., 1873, 168—190).

Numerous field experiments, extending over four years, were made upon light soil in Cumberland The following series will give a fair idea of the results. The potatoes in this series were grown year after year on the same land. The yield is given in tons per acre.

Manures.	1868.	1869.	1870.
No manure	5·92	4·71	3·21
Superphosphate	7·15	5·07	4·04
Superphosphate and potassium chloride	7·43	6·68	6·75
Superphosphate and ammonium sulphate	—	5·39	4·52
Superphosphate, ammonium sulphate, and potassium chloride	—	9·10	8·16
Superphosphate, ammonium sulphate, potassium chloride, and magnesium sulphate...	—	8·20	7·15

Both the quantity of the crop and the size of the tubers were here increased by the application of potash. It appears from several experiments that the yield of potatoes diminishes when the crop is grown repeatedly on the same land, even when liberally manured. In the above experiment the falling off is much less where potash was applied. On land in high condition no distinct effect was produced by any additional manure. Potash added to a small dressing of dung increased the crop, but with a full dressing it was useless. Heavy dressings of soluble manures appear to have a prejudicial action; commercial sulphate and chloride of potassium are therefore preferable to kainite, of which large quantities must be used if any considerable amount of potash is to be applied. Common salt was found quite incapable of replacing potassium chloride. The author recommends as a potato manure, superphosphate 6½ cwts., commercial "muriate of

potash" $2\frac{1}{2}$ cwts., and ammonium sulphate $2\frac{1}{2}$ cwts., these quantities to be applied per acre without dung. This compound potash manure improves the keeping quality of the potatoes, but is no preventative against disease, freedom from which depends much on cultivating only recent varieties.

T. Ferguson (*ibid.*, 102—107) experimented on the same subject upon a light loam in Coupar-Angus in 1871. His results are generally similar to the above, but he obtained larger products from manures supplying phosphates and nitrogen only. Potassium sulphate was found to be superior to potassium chloride.

R. W.

Waste Products. By A. H. Church (Trans. Highland Agri. Soc., 1873, 220—235).

Various waste residues are described of which the following seem the most important. Fresh blood contains about 3 per cent. potential ammonia, 5 per cent. potash, and 1 per cent. phosphoric acid. Dry blood is five times as rich. Blood may be utilised as a manure by mixing with dry peat, or by coagulation with 3 per cent. of quicklime, and then drying. Flesh, fish, hair, and wool are best prepared for manure by heating with steam under pressure; they are then so disintegrated that they may be dried and powdered. Horn when gently roasted may also be powdered. Glue refuse is a slimy matter, containing in the fresh state 1·75 per cent. nitrogen, and when dry 3·8 per cent. "Trotter-scutch," a refuse of skin and hair from tanneries, is a cheap manure, containing in the fresh state 3·58—7·60 per cent. of potential ammonia. Refuse hops from breweries contain when fresh 1·91, and when dry 4·20 per cent. potential ammonia; they are best added to compost heaps. The deposits from fermenting liquors are always highly nitrogenous. Sugar-boilers' scum contains both nitrogen and phosphates; the scum from beet-root syrups appears the most nitrogenous, containing when dry 4—6 per cent. potential ammonia. The liquors obtained by "retting" flax and hemp are nitrogenous, the solid contents yielding 2·7—4·0 per cent. potential ammonia. Spent galls are used as manure; they contain, however, in a hundred parts only 1·32 potential ammonia, ·90 potash, and ·17 phosphoric acid. Analyses of wheat embryos, separated in Child's decorticating process, and of giant puff-balls (*Lycoperdon giganteum*), weighing 1—2 lbs. a-piece, were as follows:—

	Wheat embryos.	Giant puff-balls. Fresh.	Giant puff-balls. Dry.
Water	12·53	90·87	—
Albuminoïds	35·70	5·48	66·78
Oil	4·18	·90	11·00
Cellulose, &c.	41·83	2·10	14·78
Ash	5·76	·63	7·44
	100·00	100·00	100·00

The nitrogen in the puff-ball is all calculated as albumin; a part,

however, existed as nitrates. The ash-analysis of the puff-ball was as under:—

P_2O_5.	K_2O.	Na_2O.	CaO.	Fe_2O_3.	SiO_2.	Undetermined.		
46·19	35·48	6·95	2·47	1·08	0·66	7·17	=	100

R. W.

Composition of some of the kinds of Guano now in the Market. By T. ANDERSON (Transactions of the Highland Agricultural Society, 1873, 316—326).

Analytical Chemistry.

Remarks on some Peculiarities observed during Researches on Spectral Analysis. By LECOQ DE BOISBAUDRAN (Compt. rend., lxxvi, 1263—1265).

AFTER noticing that in the spectral examination of a solution by means of the induction spark, the exterior platinum wire should be positive and the solution negative, the author remarks—

1. That certain solutions, such as silver nitrate, at first give only the air spectrum, even when they are negative; this difficulty can be overcome by moistening the exterior platinum wire with the solution.

2. The presence of metallic particles in the interpolar space renders the air spectrum more feeble, especially in that portion of the spectrum to which the bands proper to the metal belong; this is probably the reason why the violet nitrogen bands are more developed in a sulphate of sodium spectrum than in that of potassium sulphate.

3. The exterior wire may be brought nearer to the surface of the liquid when it is positive than when it is negative, the liquid in the latter case tending to come in contact with the wire.

4. The projection of minute drops of the liquid, its *pulverisation*, increases rapidly with the length of the spark. It varies, moreover, considerably with the nature of the liquid; thus, although generally feeble with the metallic chlorides, it is considerable with concentrated solutions of the chlorides of tin and bismuth. Again, it is very feeble with fused potassium sulphate or carbonate, whilst the nitrate is so dispersed that the study of its spectrum is rendered difficult.

5. The state of dilution of the solution influences the relative intensity of the rays; for instance, in a concentrated solution of $CaCl_2$, $BaCl_2$, $CuCl_2$, &c., the spectrum is complex, containing the bands proper to the chloride, the metal, and the oxide, and dilution tends to increase the intensity of the spectrum of the oxide, and diminish that of the chloride; the addition of hydrochloric acid, on the contrary, reverses this effect. When the spectrum of the concentrated solution is simple, as is the case with the salts of the alkalis, $ZnCl_2$, $CdCl_2$, &c., notable variations are sometimes observed in the relative intensity of the bands, thus lithium chloride in concentrated solution gives the

orange band stronger than the red, but on dilution the red becomes the stronger. With zinc chloride the red band, β 636·1, becomes feebler than the blue bands, γ 472·1, and δ 468·1, when the solution is diluted, and with cadmium chloride, the red band, γ 643·8, becomes more feeble than the blue δ 467·7.

6. When, after long heating in a gas flame, there remains only a trace of the substance on the platinum wire, the last band to disappear is not always that which was originally most brilliant; thus with baryta the green-blue bands remain visible longest.

7. Some metals, such as platinum, palladium, and even silver and copper, do not readily give the bands when in a compact state, but yield fine spectra when finely divided. In certain instances the author recommends alloying the metals for this purpose with lead, which is especially applicable in the case where the metals are readily precipitated from their solutions by zinc or by the voltaic current. He adds a salt of lead to the solution, and after reduction fuses the spongy metallic deposit. In testing for thallium and indium, it is necessary to leave the solution in contact with the zinc for a considerable time in order to insure the precipitation of these metals. Copper, on the contrary, is amongst the first to be precipitated.

C. E. G.

Note on Quantitative Spectrum Analysis. By JANSSEN (Compt. rend., lxxvi. 711—713).

REFERRING to the paper of Messrs. Champion, Pellet, and Grenier on the spectro-sodiometer (page 934 of this volume), the author remarks that he himself, in a communication made to the French Academy, the 7th November, 1870, proposed two methods for the quantitative estimation of sodium, the one taking the intensity of the coloration imparted to the flame, the other the time during which the coloration lasts, as a measure of the quantity of sodium which is contained in the substance under examination.

R. S.

On the Spectrum of Chlorophyll. By J. CHAUTARD (Compt. rend., lxxvii, 596).

THERE is one band at the red end of the spectrum of chlorophyll which suffices to distinguish the substance under all conditions, owing to the following properties:—

Sensibility: being sharply defined, fixed in position, and exhibited with very weak solutions.

Certainty: since under the influence of alkalis it is divided into two bands, which character is exhibited by no other colouring matter.

Generality: since it appears wherever chlorophyll exists, whether pure or altered.

Chlorophyll exists in three different conditions, the first in young leaves, the second in leaves fully developed, the third in dead leaves.

The author considers chlorophyll much more stable than is generally supposed. He says that "it resists the action of iodine, of alkalis, and of the digestive organs, and preserves, if not its primitive composition and habits, at least the characters which permit it to be detected in the most various and complex mixtures, and after a considerable lapse of time."

Its solution in oil resists in a remarkable degree the action of air and light. M. J. S.

Action of Iron Salts on Pyrogallic Acid. By E. JACQUEMIN (Compt. rend., lxxvii, 593—596).

PYROGALLIC acid added to a ferrous salt perfectly free from ferric salt, does not give the blue colour which is mentioned by most authorities, but yields a white opalescence, which, on exposing the solution to air, gradually disappears, whilst the blue colour due to a trace of ferric salt makes its appearance. Pyrogallic acid is a more delicate test for ferric salts than even a sulphocyanate.

When the ferrous salt contains 2 per cent. of ferric salt, the blue colour at first produced changes in a few minutes to green and then to red. If as much as one equivalent of ferric salt is present with three of ferrous, the red solution gradually becomes turbid, and during the first day purpurogallin is precipitated; during the second day a mixture of purpurogallin with iron tannomelanate, and on the third day the tannomelanate alone. These slow changes are caused by the absorption of oxygen from the air; but if, after the separation of the purpurogallin, an excess of ferroso-ferric salt be added, the oxidation takes place rapidly. In the latter case the brown liquid is precipitated by ammonia, but if traces of ammonia be added to the liquid during the slow process of oxidation, a deep blue-black or purplish-blue colour is obtained. Addition of a very little more ammonia changes the colour to violet, and then through amethyst to bright red. The blue colour obtained with traces of ammonia is far more permanent than purpurogallin-blue, but finally oxidises, yielding a black precipitate of iron tannomelanate. Similar phenomena are observed when dilute ferric chloride is used in place of ferroso-ferric sulphate. The red obtained with excess of ammonia is reconverted into blue by slight acidification with acetic acid. Excess of acid changes the colour to green. The addition of ammonia increases the delicacy of the pyrogallic test for ferric salts. One cubic centimeter of a solution containing 0·000005 gram of ferric chloride gives a distinct amethyst coloration.

The addition of pyrogallic acid to the brown solution of ferric ferricyanide gives a blue precipitate soluble in pure water. From its possessing a very pure tint, and from its behaviour with ammonia, the author concludes that the pyrogallic acid has in some way entered into its constitution, since otherwise a brown colour due to the oxidation of the acid would contaminate the blue.

M. J. S.

A Method for Comparing Different Kinds of Gunpowder.
By M. DE TROMENEC (Compt. rend., lxxvii, 126—128).

THE author observes that the present methods of testing gunpowder are insufficient, and that they are especially fallacious in the comparison of powders differing greatly in their physical characters. He proposes to explode the powder under circumstances in which it is restrained from performing any work, to determine the heat thus produced, and express the force of the powder in kilogrammeters. The apparatus used consists of a strong steel cylinder holding about half a litre, in which 5 grams of the powder are ignited by electricity. The heat produced is determined by an ordinary water-calorimeter.

In the same number of the *Comptes rendus* Messrs. Roux and Sarron describe an identical method and apparatus, and investigate the corrections for radiation and the slow conduction of heat by the walls of the explosion chamber. They also weigh the gases produced, and propose to attempt the determination of their volume as a necessary element in the calculation of the dynamic effect.

M. J. S.

Methods of analysing Natural Phosphates.
By C. MÈNE (Compt. rend., lxxvii, 430).

IF the analyst does not separate the silica before determining phosphoric acid, it will come down on the addition of ammonia (as citric acid fails to hold silica in solution), and may, the author thinks, be mistaken for ammonio-magnesic phosphate.

R. W.

Separation of Uranium Oxide from Phosphoric Acid.
By E. REICHARDT (Arch. Pharm. [3], ii, 232—234).

THE author proposes to modify his method of separation by dissolving the uranium phosphate (in the accumulated residues from the phosphoric acid determination) in a large excess of sodium carbonate and precipitating the phosphoric acid with magnesia mixture. Old residues are best dissolved first in hydrochloric acid. Any ferrous oxide should be peroxidized and the sodium carbonate added to a dilute solution till a clear solution is obtained. The precipitated ferric hydrate is filtered off previous to adding the magnesia mixture. A little more ammonium chloride may also be added if the liquid should remain turbid. Ammonio-magnesium phosphate is filtered off as usual. The filtrate is rendered acid by means of hydrochloric acid, boiled till no more carbonic acid is left, and the uranium oxide precipitated by ammonia. The precipitate is readily washed out and may at once be re-dissolved in acetic acid.

W. V.

Separation of Phosphoric from Molybdic Acid.
By E. REICHARDT (Arch. Pharm. [3], ii, 234).

ON the addition of sodium carbonate to phospho-molybdenum residues, molybdic acid is readily dissolved. Any metallic oxides precipitable

by sodium carbonate are filtered off, and magnesia mixture added to the filtrate as long as a precipitation takes place. The ammonio-magnesium phosphate removed, sulphuretted hydrogen is passed through the alkaline filtrate. On subsequently acidulating with hydrochloric acid, molybdic sulphide is precipitated, and can be worked up as usual into ammonium molybdate either by roasting or evaporation with nitric acid previous to dissolving in ammonia and crystallisation.

W. V.

Analysis of Nickel and Cobalt Ores, Speiss and other Metallurgic Products; an easy and accurate method of Separating Zinc from Nickel and Cobalt. By R. FRESENIUS (Zeitschr. Anal. Chem., xii, 66—73).

IN the analysis of the ores, &c., of nickel and cobalt, great differences occur, which are due to imperfect methods of separation. In a particular case the author found 19·63 per cent. of nickel and cobalt, while other chemists found 21·55—22·12 and even 25·46.

An account is given of the methods by which these numbers were obtained, and the author shows that the substance contained 2·24 per cent. of alumina, iron, lime, and magnesia, which accounts for the difference of results.

The author's method contains no new process of separation. It consists essentially in dissolving the substance in aqua regia, precipitating with sulphuretted hydrogen, filtering off any precipitate, oxidising the filtrate with nitric acid, and adding excess of ammonia to precipitate the iron. Care must be taken to see that the iron precipitate contains no nickel. The filtrate is acidified with acetic acid, and after addition of acetate of soda, treated with sulphuretted hydrogen, by which means the nickel and cobalt are obtained as sulphides. These sulphides are dissolved and precipitated with caustic potash; the oxides obtained are reduced in a stream of hydrogen, and the metals weighed. The metals are re-dissolved and the solution treated with ammonia and carbonate of ammonia, by which means generally a little precipitate of iron and alumina is obtained, while the silicic acid is left undissolved. This process is repeated with the precipitate, and the necessary subtraction then made from the weight of the metals previously obtained.

If the ores or other substance contain zinc, it will be precipitated with the nickel and cobalt. In this case the solution of the sulphides is evaporated to a small bulk, and pure, finely crystallised sal-ammoniac added (about 5 grams of sal-ammoniac to 0·2 gram of zinc oxide); the mass is then dried on the water-bath and carefully heated till all the sal-ammoniac, and with it the zinc, is removed.

When chloride of nickel or cobalt is heated with sal-ammoniac, not the slightest loss is occasioned, while zinc is totally expelled.

To separate nickel from cobalt: If the nickel is in excess, the cobalt is removed as nitrite of potassium and cobalt; if the cobalt is in excess, the solution of the chlorides is treated with potassium cyanide in excess, pure caustic potash added, and the nickel precipitated by bromine.

Comparison of the Processes for Estimating Alcohol.

By A. KRAFT (J. pr. Chem. [2], vii, 228—247).

THE author has made experiments upon mixtures of alcohol and water, and upon various wines, for the purpose of comparing the following processes:—

1. By the vaporimeter.
2. By distillation.

The determination of the alcohol in the distillate was made by Kappeller's alcoholometer, by the pycnometer, and by Mohr's balance.

3. By Balling's saccharimetric method.

With carefully made instruments the first two processes give closely concordant results. The third, which consists in determining the specific gravity of the alcoholic liquid by a saccharimeter, then evaporating to a small bulk, re-diluting to the original weight, and applying the saccharimeter, is not trustworthy. The percentages of alcohol obtained in the author's experiments with this process were from ·86 to 2·03 higher than those given by distillation.

W. A. T.

Improvements in the Determination of the Amount of Juice in Sugar-Beet by means of Polarisation.

By FERDINAND JICINSKI (Dingl. polyt. J., ccviii, 452—460).

THE author formerly recommended that the juice be weighed; he has found by experiment, however, that as determinations of the amount of sugar by polarisation in weighed and measured samples do not differ from each other more than 0·1 per cent., it is a matter of indifference which method be employed. It has also been found advisable in extracting the juice to digest the pulp four times with cold water; if water of 60°—80° be used, two digestions are sufficient. The smallest quantity of juice found by Stammer amounted to 92 per cent. The maceration of the roots should not be conducted on the filter, but in a beaker. The liquid is then poured into the funnel, which should contain a platinum cone. If some of the pulp be poured into the filter along with the liquid, the cone serves to prevent it from passing through. It is unnecessary to measure the amount of water used in extraction; the filtrate should amount to 90—95 c.c., and must be accurately measured.

The author finds that, on evaporation of the juice, if the temperature reach 105°, decomposition begins to take place. The evaporation should therefore be conducted at 100°, and when the residue is partially dry, the temperature should not be allowed to rise above 90°. The juice may be dried in three ways:—1st. By mixing it with a weighed amount of sand and evaporation. 2nd. By drying it, moistening several times with alcohol, and finally evaporating to dryness. 3rd. By evaporation in a platinum basin. The first of these three methods always shows a higher percentage of water.

W. R.

Valuation of Commercial Anthracene. By Dr. PAUL and A. J. COWNLEY (Chem. News, xxviii, 175).

ANTHRAQUINONE, formed by oxidising anthracene with a solution of chromic anhydride in glacial acetic acid, is proposed as a basis for the valuation of anthracene. 100 parts of good anthracene, whose absolute purity was not however guaranteed, furnished 117 parts of anthraquinone. The melting point of the latter is placed by the authors 3° higher than it is generally supposed to be.

B. J. G.

Tests for Solanine. By O. BACH (J. pr. Chem. [2], vii, 248—251).

THE solanine was obtained from potato-shoots by the usual process. The author has examined the reactions described as characteristic of solanine, with results differing to some extent from those obtained by other chemists. Thus, contrary to statements occurring in some handbooks of toxicology, he found that pure solanine gave with concentrated nitric acid a colourless or slightly yellow, not a blue solution, which in ten or twelve hours deposited colourless flocks.

The most suitable test for the recognition of small quantities of solanine and solanidine he considers to be a mixture of equal volumes of concentrated sulphuric acid and alcohol. On introducing a trace of solanine into the mixture, whilst still warm, a beautiful red colour is developed, which lasts some time. One advantage of this test is that morphine, even in considerable quantity, does not affect the colour, a circumstance of some importance when the process of Stas is employed for the detection of alkaloïds, morphine and solanine being the only alkaloïds which are extracted by ether from acid, as well as from alkaline solutions.

The author finds that the solanine in sprouted potatoes resides only in the peel, and in that part of the tuber from which the shoot arises.

W. A. T.

Estimation of Aniline Colouring Matters by means of Sodium Hyposulphite. By A. STAMM (Bull. Soc. Chim. [2], xix, 124—127).

WHEN an aqueous solution of magenta or other aniline colour is mixed with a solution of sodium hyposulphite (Schützenberger's hydrosulphite), the aniline salt is instantly reduced, and the solution decolorised. This reaction the author proposes to utilize for the estimation of the tinctorial power of the various coloured aniline derivatives.

The strength of the hyposulphite solution is ascertained by titrating it against a known weight of the pure crystallised aniline colour, after which it is used as an ordinary volumetric solution; some care, however, is required in the manipulation of this reagent, owing to the rapidity with which its absorbs oxygen. The operations must be conducted in a closed vessel, from which the air has been expelled by a current of carbonic anhydride, and since the decolorisation takes place

only at 100°, the liquids under examination must be raised to ebullition.

The author finds that one molecule of the various aniline colours, whose composition is accurately known, requires for complete decoloration the same quantity of hyposulphite as that which is required to reduce two molecules of ammoniacal copper sulphate. From this circumstance it is possible, if the law obtains universally, to deduce approximatively the molecular weight of any well-defined aniline colour. Thus the "violet de Paris" and Hofmann's violet gave absolutely identical results; for the "vert de Paris," the molecular weight, 460, was calculated from the experimental results, a number which corresponds very well with the formula, $C_{20}H_{16}(CH_3)_3N_3.2(CH_3Cl) + H_2O = 462$, assuming that it has a composition analogous to that of "iodine green."

J. W.

On the Different Methods employed for the Quantitative Estimation of Caffeine. By R. Weyrich (Zeitschr. Anal. Chem., xii, 104—111).

The author has examined the methods proposed by Mulder, Péligot, Claus, Zöller, and Lieventhal.

Péligot's method consists essentially in precipitating the tea-infusion with basic lead acetate, with addition of a very little ammonia, and after careful washing, decomposing the filtrate with sulphuretted hydrogen. After a second filtration, the caffeine crystallises out of the liquid. Any caffeine that remains in the mother-liquor is estimated by titration with tannin.

The objections to the method are that it requires a large amount of material to work with, and is therefore inapplicable when only a small amount is available for analysis. The titration is untrustworthy, because the tannin carries down other matters besides caffeine, and thus gives results too large. On the other hand, it is possible that less than the real amount of caffeine may be obtained, because lead sulphide has the property of taking down with it such matters as alkaloids, and of retaining them when washed.

The method of Claus consists in exhausting the leaves with ether, shaking up the ethereal solution with water containing sulphuric acid, supersaturating the acid caffeine-solution with calcined magnesia, evaporating to dryness, and exhausting the dried residue with ether.

This method is very similar to Mulder's, and gives tolerably equal results. The source of error is that the whole of the caffeine is not always extracted in the shaking up of the first ethereal solution with acidulated water.

Zöller's method is to boil the powdered tea-leaves with common sulphuric acid a little diluted. Water is then added, and the liquid neutralized with hydrated oxide of lead, evaporated to dryness, and the residue exhausted with alcohol of 85 per cent. After filtration and evaporation to dryness, the caffeine is extracted with ether, and on distilling off the ether the caffeine is left.

But the caffeine thus obtained is very impure, and besides it is not impossible that when thus heated for some time with an acid, it may be partly decomposed, and in that case the result will be below the real percentage. Lieventhal boils the powdered tea for a minute or two with chloroform. After cooling, the mass is washed till the chloroform flows through colourless. The filtrate is distilled and the residue boiled with distilled water and evaporated to dryness. The caffeine then remains behind, but is not colourless.

The author does not think that the chloroform penetrates into the tea, even when finely powdered, sufficiently to extract all the caffeine; moreover, other substances, as well as the caffeine, pass into solution.

Mulder's method is preferred by the author to all others, on account of its simplicity, and more especially because the caffeine is obtained by it perfectly pure in colourless crystals.

Raw coffee-berries are dried at 100°, and then finely powdered. Tea can be used just as it is found in commerce. A weighed quantity is boiled with distilled water; in the case of coffee three times, each of an hour's duration; in the case of tea, as long as the filtrate comes through coloured. By this means all the caffeine, as well as some other matters, passes into solution. The filtrate is evaporated on the water-bath to the consistence of a syrup, and then, after being mixed with calcined magnesia to strong alkaline reaction, evaporated to dryness. The finely powdered residue is digested for several days with ether, filtered, and the residue again treated with ether, and finally washed with ether upon the filter as long as a drop of the filtrate placed on a watch-glass leaves a residue of caffeine. The ether is then distilled off, and the pure caffeine remains. The author prefers chloroform to ether, as caffeine is more soluble in the former, and the operation is thus shortened.

G. T. A.

Separation and Detection of Strychnine in Judicial Cases. By J. ST. CLAIR GRAY and J. B. LYMAN (Zeitschr. Anal. Chem., xii, 125).

GRAY's method is to rub up the substance in a mortar with distilled water, mix it with excess of acetic acid, and after digesting it for 24 hours at 27°, submit it to dialysis, the dialyser floating on a quantity of water equal to ten times the volume of the liquid.

After 48 hours the liquid is evaporated down to a drachm, acidified with acetic acid, and repeatedly shaken at intervals of five minutes with double the quantity of chloroform, until the latter on evaporation leaves no residue.

The watery solution is mixed with ammonia in excess, shaken again for five minutes with four times its volume of chloroform, and the latter evaporated upon watch-glasses so as to prevent the accumulation of the alkaloid in any one spot. The residue is then moistened with a drop of concentrated sulphuric acid, and if it remains colourless is examined by Otto's colour-test. If not colourless, it must be warmed with a few drops of sulphuric acid, saturated with ammonia, and again

treated with chloroform. Acetic acid is preferable to all others, because it coagulates albuminous matter, does not convert starch into sugar, is easily removed, and forms the most soluble strychnine salts.

The colour reaction is also easily produced by placing the sulphuric acid solution of strychnine on platinum foil connected with the negative pole of a one-celled battery, while the positive pole is dipped into the solution.

The physiological action of the alkaloïd on frogs was found to be much increased by drying them with a towel and placing them on blotting paper under a bell-jar for 24 hours, so as to get rid of moisture. In animals thus treated, the thirty-thousandth of a grain produced the usual convulsions in fifteen minutes.

Lyman states that in case of any impurities, potassium permanganate, silver oxide, and hydrated peroxide of manganese, are preferable to compounds of chromic acid, only that in the case of permanganates the appearance of the purple colour alone is not decisive, as a similar one is produced by other organic matters; but in the latter case it changes to a yellowish tint, while in the strychnine alone it passes into a bright red.

G. T. A.

Analysis of Cheese. By ALEX. MÜLLER (Zeitschr. Anal. Chem., xii, 111—117).

EXCEPT in special cases, the analysis of cheese is limited to the estimation of water, fat, protein, milk-sugar, and inorganic constituents.

In the case of new cheese, the author dries the finely divided mass over sulphuric acid at a somewhat low temperature, and then extracts the fat by means of ether. The residue is then dried at a gradually increasing temperature and weighed. The difference between the original weight and the sum of the fat and the residue from which the fat has been extracted, gives the quantity of water.

The porous, easily pulverised residue is particularly well fitted for the estimation of nitrogen (from which the protein is calculated by multiplication by 6·25), and the inorganic constituents.

The difference between the dried substance freed from fat, and the sum of the protein and ashes, gives with sufficient accuracy the quantity of milk-sugar.

In the case of old cheese, the fat is estimated as above, but attention must be directed to the presence of lactic acid, fatty acids, and possibly ammonia-compounds, and hence the analysis becomes more difficult. Methods are given only for the determination of ammonia and nitrogen.

G. T. A.

Technical Chemistry.

Polychromic Photography. By L. VIDAL (Compt. rend., lxxvii, 340—342).

THIS method is merely an extension of the "carbon" process. It consists in producing a series of partial impressions, each consisting of one colour, and transferring these in succession to the same surface. The process is carried out as follows:—

Several negatives are obtained, and each is then covered with an opaque resist in those parts which in the original view do not contain the particular monochromatic tint which it is desired to produce. This is done by hand, but requires no great skill. From each of these negatives as many positives as may be desired are then printed by the ordinary carbon process, substituting for black the required monochrome. The provisional support, on which these partial positives are printed, consists of parchment paper soaked in a cold, saturated, alcoholic solution of shellac. The developed image is alumed, coated with a thin film of gelatin, and allowed to dry. To transfer one of these images to its final support, the surfaces are placed in contact with one another under water, then removed, pressed lightly between blotting-paper, and allowed to dry gently, still in contact. A short immersion in alcohol then softens the shellac; the parchment paper is removed; and the monochrome left adhering to the permanent surface. Second and third monochromes of different colours are then transferred to the same surface by a repetition of the process, exactly in the way that a chromolithograph is printed. The transparency of the provisional support obviates all difficulty in making the different colours register.

M. J. S.

Berlin Water-supply and Town Purification. By A. MÜLLER (Landw. Versuchs-Stationen, xvi, 241—273).

THE author describes, in general terms, the condition of the River Spree before its entrance into Berlin, and the state of impurity it acquires while passing through the town, also the character of the well water which forms part of the town supply. All attempts to utilise night soil in a solid state have failed; equal failure has attended the efforts to purify sewage by chemical means, but irrigation upon sandy soil has proved successful. Thorough drainage of the town, with sewage irrigation, is recommended. Grass, mangold, and maize have proved most successful sewage crops; the vegetable produce contains nitrates in considerable quantity. Besides many well-known facts, the author remarks that when the soil is insufficiently aërated, the sewage deoxidises and removes in solution a large amount of ferric oxide; that under the same conditions the amount of sulphuric acid in the sewage falls, ferrous sulphide being probably produced. On the other hand, with intermittent filtration, the organic carbon, nitrogen, and sulphur of the sewage are all oxidised, and more carbonic, nitric, and

sulphuric acid are found in the drainage-water than in the sewage, and the former is harder than the latter. When, however, a crop is grown, the drainage-water becomes very pure.

Analysis can never infallibly ascertain the wholesomeness of drinking water. The author considers the capacity of the water to grow fungi as a better test (compare however this Journal, 1871, 66). Dilute solutions of urea in pure water were kept for many months; only a very little ammonia, and no nitric acid or fungus, was produced. When the experiments were repeated with water from the town supply, much more ammonia was formed, together with nitric acid, and a growth of mould. In pure solutions ammonia does not change into nitric acid; the presence of alkalis or sugar, in light or darkness, is unable to effect the conversion. A decoction of linseed of similar strength to sewage did not yield nitric acid. On the other hand, sewage, and many well waters, rapidly form nitric acid on keeping. The author thinks that in these cases a particular ferment is present, and proposes to ascertain the presence of this ferment by adding urea to a suspected water, and noting the result.

R. W.

Water-filters of Moulded Charcoal. By JULIUS MÜLLER (Dingl. polyt. J., ccviii, 450—452).

IT appears from experiments made by the author that filtration through filters of moulded charcoal is insufficient to remove germs and spores from impure water; on exposure to the sun, a green variety of *Prococus* appeared in filtered water as soon as in that which had not been filtered.

W. R.

Manufacture of White-lead. By K. v. WEISE (Dingl. polyt. J., ccviii, 434—439).

WHITE-LEAD manufactured by the German method is, according to the author, superior in colour and "body" to either the Dutch or French made article. This method consists in passing acetic acid and water vapours into a chamber containing thin plates of lead, and subsequently introducing air and carbon dioxide. The advantage of this method is that the process can be easily regulated. The normal composition of white-lead is stated to be that expressed by the formula $2(PbO.CO_2) + PbO.H_2O$. An excess of carbonate makes a white-lead which possesses little "body;" the carbonate tends to crystallise, but the "body" depends upon the smallness of the particles.

Sometimes very finely divided metallic lead is found in white-lead; this gives a grey colour to the sample. It also occasionally happens that specimens appear partly coloured yellow or red; this is caused by the presence of lead oxide (not hydrate). The following analyses show the composition of good and bad white-lead:—

	Lead oxide.	Carbon dioxide.	Water.
1. Best quality	86·80	11·16	2·00
2. Second „	86·24	11·68	1·81
3. Third „	86·03	12·28	1·68
4. Bad white lead	84·69	14·10	0·93
5. Very bad „	83·47	16·15	0·25
6. Containing coloured patches,.	93·70	5·31	0·90

Now, 5·31 CO_2 combine with 26·91 PbO, and 0·90 H_2O with 11·15 PbO: consequently the last sample of white-lead contained 93·90 — (26·91 + 11·15) = 55·64 pts. of anhydrous lead oxide, which was the cause of the coloration. M. M. P. M.

Behaviour of Fire-clay in contact with Iron Slag at a High Temperature. By CARL BISCHOF (Dingl. polyt. J., ccviii, 445—450).

THE action of iron slag on the Hessian, Mülheim, Grünstadt, and Belgian fire-clays is to cause them to fuse at a temperature at which platinum ceases to be ductile. To apply the test, a small cylinder is formed of the fire-clay mixed with the desired proportion of slag; when the cylinder loses shape, a comparison of the experiments may be made. With normal Hessian fire-clay, 1 per cent. induces this change of form at the fusing point of platinum. Grünstadt, Mulheim, and Belgian fire-clays require from 5·7 per cent. Zoltitz and Laaran No. I fire-clay fuse respectively with 14 and 13 per cent. 8 per cent. of iron slag produces the same effect as 18 per cent. of glass. Garnkirk fire-clay required 8 per cent.; Laaran No. II, 6 per cent. The former of these contains sand; the author attributes its greater infusibility to the action of the silica on the iron. A trial was made with two different slags, one, containing 54 per cent. of lime, obtained in the Bessemer process for grey iron; the other, 41 per cent. of lime, obtained in the manufacture of white iron. The latter exhibited less tendency to render fire-clay fusible. The author recommends that in every case a positive experiment should be made. W. R.

Composition and Technical Properties of Coals. By CARL HILT (Dingl. polyt. J., ccviii, 424—434).

THE author adopts the ratio between the amount of volatile matters and coke as the basis for a technical classification of coals. From a number of analyses he deduces the following numbers:—

1. Anthracite: The ratio of volatile matter to coke varies from 1 : 20 to 1 : 9 = 5 to 10 per cent. volatile matter.
2. Flint coal. The ratio of volatile matter to coke varies from 1 : 9 to 1 : 5·5 = 10 to 15·5 per cent. volatile matter.
3. Caking coal. The ratio of volatile matter to coke varies from 1 : 5·5 to 1 : 2 = 15·5 to 33·3 per cent. volatile matter.
4. Caking gas coal. The ratio of volatile matter to coke varies from 1 : 2 to 1 : 1·5 = 33·3 to 40·0 per cent. volatile matter.
5. Gas coal. The ratio of volatile matter to coke varies from 1 : 1·5 to 1 : 1·25 = 40·0 to 44·4 per. volatile matter.

6. Gas coal. The ratio of volatile matter to coke varies from 1 : 1·25 to 1 : 1·11 = 44·4 to 48 per cent. volatile matter.

No. 1 includes the varieties of ordinary anthracite.

No. 2 includes such coals as the "smokeless steam coal" of Cardiff.

No. 3 includes the varieties of coal used for general manufacturing purposes.

No. 4 is a good gas coal, but yields little coke, and this of too porous a nature.

Nos. 5 and 6 are chiefly used in open stoves; they burn with a bright flame, accompanied by a considerable quantity of smoke.

M. M. P. M.

Continuous Process for Purifying Coal-gas from Sulphur and Ammonia. By A. VERNON HARCOURT and F. W. FISON (Chem. News, xxviii, 175).

AFTER "oxide" has been used twenty or thirty times in removing sulphur from gas, it becomes "spent," and is then sold to the vitriol maker. The new process prevents this deterioration of the oxide, besides removing the ammonia from the gas without the use of "scrubbers," and enabling the gas manufacturer himself to obtain sulphur containing but little impurity, and ammonia as sulphate. The method consists of a round of operations. The oxide is moistened with a solution of ferric sulphate before introducing it into the purifier The ammonia of the gas entering the purifier is converted into sulphate, and the ferric oxide formed fixes the sulphur. The oxide after removal from the purifier is washed with water, which dissolves the ammonium sulphate, and the residue is boiled with dilute sulphuric acid, which dissolves ferric oxide, forming ferric sulphate, to be used with a fresh charge, and leaves the sulphur. In practice it is found best to proceed thus: the oxide taken from the purifier is washed with water, and the liquor evaporated to obtain ammonium sulphate, a little sulphuric acid being first added. The oxide is then boiled successively with four dilute solutions of sulphuric acid, *a*, *b*, *c*, *d*, each weaker than the preceding, and finally washed with water. Solution *a* is used in moistening a fresh charge of oxide before it enters the purifier. Solution *b* becomes solution *a* when more oxide is ready for extraction. Solution *c* then takes the place of *b*, and *d* of *c*, the water used at the end of the previous treatment becoming the solution *d* of the new one.

B. J. G.

The Removal of Sulphur from Coke.
(Dingl. polyt. J., ccviii, 463)

DR. HOFMANN has discovered that an addition of acid manganese chloride to coke in extinguishing it, removes the sulphur in the state of sulphuretted hydrogen. In a large Rhenish puddle-work a liquor consisting of a solution of manganese and calcium chlorides has been employed for this purpose.

W. R.

Use of Sodium Aluminate in Calico-printing.

By A. KIELMEYER (Dingl. polyt. J., ccvii, 203—205).

In calico-printing, a strongly-woven piece of cloth is inserted between the woollen or india-rubber piece on the one side, and the piece of calico to be printed on the other, for the purpose of taking up the print-colour penetrating through the calico, and it must, therefore, pass through a portion of the hot chamber to be dried. The object of this intermediate piece is to furnish a perfectly clean, equal, even, and elastic layer for the piece to be printed to rest upon. This piece of cloth may generally be used two or three times before a cleansing is necessary.

In printing with aniline black, it was found that the cloth layer soiled by the black could not be completely cleansed by the succeeding bleaching operation, and that the fibre of the thread had suffered. In English print-works, the above difficulty has been overcome by immediate immersion of the piece in cold water after each operation, an apparatus for the purpose being annexed to the printing machine. The development of the black is prevented by the immersion in cold water.

The author has, for some time, advantageously used for the same purpose sodium aluminate, thickened to a paste with starch burned brown: this paste he uses under the aniline black in printing. The alkaline portion of this paste renders a development of the black impossible; also where the black and sodium aluminate come in contact, aluminium hydrate is separated out, and acts as a "reserve," effectually cutting off contact of the black with the cotton fibre. The sodium aluminate is used to prepare the intermediate pieces of raw cloth above referred to (used as "runners" for the calico in the printing operation), in the following way:—

After singeing, the piece is treated twice with a cold solution of sodium aluminate at 4° to 5° Baumé, and is then left for two hours rolled up, the aluminate being thereby distributed uniformly throughout the fabric. It is finally dried on the cylinder. Thus treated a piece may serve as a layer under the print during two to three operations before cleaning. Before bleaching (when too much soiled for further use without this), these pieces are to be washed, laid in hydrochloric acid of 2° Baumé, and again washed. For heavy patterns, the prepared piece can only be used once, and for very heavy goods, as for instance pieces with aniline black grounds, the solution of aluminate must be used at 10° Baumé.

After the bleaching, not the slightest trace of the black pattern is visible in pieces used as layers, when treated as described. The fibre of the goods is also not at all contaminated with alumina. Moreover the pattern on the backs of the pieces of goods is much more faintly developed when a prepared "runner" or intermediate piece is used, than when the latter is unprepared.

It may be added that the author has tried sodium carbonate and acetate instead of the aluminate, but without success, these salts having the power of arresting the development of aniline black, without, however, acting as a "reserve," *i.e.*, preventing the colour which penetrates the calico from also penetrating the under-piece of cotton or "runner." W. S.

Iron Liquor for Calico-Printing. By A. Kielmeyer (Dingl. polyt. J., ccviii, 439—443).

By carefully regulating the dry distillation of wood, a product may be obtained, from which an iron liquor of constant quality is easily manufactured. The usefulness of ferrous acetate as a mordaunt depends mainly on a due admixture of ferrous and ferric salts, it is therefore advisable to work with a liquor containing a certain proportion of tarry matter, which, by forming a layer on the surface, prevents the undue oxidation of the iron on the cloth.

To estimate the iron in a sample of liquor, the author evaporates 10 grams to dryness in a weighed dish, heats with a little nitric acid, and weighs as ferric oxide; the hydrometer does not give trustworthy results, owing to the presence of tarry matters.

M. M. P. M.

A New Aniline Red. By E. Ferrière (Compt. rend., lxxvii, 646).

Ammoniacal cupric hydrate is added to aniline acetate, and the mixture then saturated with sulphuric acid. A fine purple-red colour is thereby developed. The ammonium sulphate is removed by crystallisation.

M. J. S.

"Methyl Green." (Dingl. polyt. J., ccviii, 466.)

The substitution-products of rosaniline with alcohol-radicals were formerly prepared by the action of the respective iodine compounds on a salt of rosaniline. They may be more economically obtained by the direct oxidation of methyl-aniline. The products thus obtained differ from those prepared by the former process only in retaining their colour in artificial light, and are distinguished by the name "methyl violet." Another methyl group may be added by the action of methyl chloride on methyl violet, forming the compound known as "methyl green." It is more easily soluble in water than the corresponding iodine compound, gives a fresher colour, and may be boiled when in solution without decomposition. Wool may be dyed with it, without further treatment.

W. R.

Dull Varnish. (Dingl. polyt. J., ccviii, 465.)

A varnish which does not reflect light is prepared by mixing a solution of resin with some liquid in which resin is insoluble. A mixture of 3 to 5 parts of sandarac dissolved in 48 parts of ether and $2\frac{1}{2}$ parts of benzol, resembles ground glass when dry. A solution of dammar resin in benzol, mixed with ether, also gives a good dull varnish. Water renders the varnish semi-opaque. Alfred Hughes recommends the following receipt:—

Ether	560	grams
Benzol	240	,,
Sandarac	40	,,
Canada balsam	10	,,

W. R.

The "Silber-light." (Dingl. polyt. J., ccix, 79.)

THIS mode of illumination is recommended where gas cannot be had. The material used is oil, which is converted into gas before combustion takes place, whereby the combustion of the wick is greatly lessened (one wick may last a year), the accumulation of impurity is obviated, and the prevention of smell completely effected. The light is regular and uniform, and of white colour. The light with a burner $1\frac{1}{4}$ inches wide, is equal to that of 28 sperm candles, each consuming 120 grains per hour, and with one $1\frac{3}{4}$ inches wide a light is obtained equal to that of 50 such candles.

The burning apparatus consists of a row of concentrically enclosed double cylinders perpendicularly arranged at definite intervals. The innermost cylinder contains the wick between its two walls, the hollow space in the interior serving to convey fresh air to the interior of the flame. The second cylinder conveys air to the outer side of the wick, and the third contains oil, and is in direct communication with both wick and reservoir. The mouths of all these chambers are covered with a dome-shaped head, and from a suitable opening in this the gas streams forth in such a manner that it comes in contact with a current of air, and thus a complete combustion is attained.

According to the nature of the oil burnt the construction is somewhat varied in its minor details. Rape-oil or light hydrocarbon oils are mentioned.

W. S.

To Colour Brass Blue like Steel. (Dingl. polyt. J., ccviii, 466.)

THE brass, laid in a leaden vessel containing hydrochloric, and a little arsenic acid, assumes iridescent colours, and may be removed when the desired shade of blue is obtained.

W. R.

Utilization of the Residues obtained in Removing the Fat from Wool, according to Chaudet. (Dingl. polyt. J., ccviii, 465.)

THE sulphurous acid from the furnace in which the sulphur has been burnt, escapes directly into the fatty water, contained in stone receivers. After the water has become acid, it is allowed to stand for 24 hours. It then separates into three layers, the uppermost consisting of impure fat, the lowest of earthy impurities, while the middle stratum is a solution of sodic, potassic, and ammonic sulphites. This solution is concentrated by evaporation and ignited, whereby the sulphites are oxidised to sulphates, which may be purified by crystallisation The uppermost layer may be pressed in sacks to obtain the fatty acids.

W. R.

Adulteration of Peppermint-oil with Castor-oil and Alcohol. (Dingl. polyt. J., ccviii, 464.)

A SAMPLE of peppermint-oil, suspected to be adulterated, left, when evaporated on paper, a stain showing the presence of some fatty oil.

The whole of the oil, amounting to fifty-five pounds, was sent for rectification by distillation with water. It consisted of 18 lbs. of pure peppermint-oil and 21 lbs. of castor-oil, which remained in the vessel; the remaining 15 lbs. consisted of alcohol. A sample prepared in these proportions did not differ from pure peppermint-oil in appearance, taste, or smell. Its specific gravity was lower than that of the pure oil, viz., 0·894 at 15° C.

W. R.

The Preservation of Yeast. (Dingl. polyt. J., ccviii, 467.)

THE yeast is washed out with cold water, and dried, first by pressure, and afterwards in a centrifugal machine. It is then removed to an exhausted vessel containing calcium chloride, and dried at a gentle heat; finally a stream of dry air or carbonic anhydride is passed over it. A dry powder is thus obtained, which may be kept hermetically sealed for some months without suffering decomposition.

W. R.

Simple Process for the Preparation of Stannic Chloride. By Prof. BRONNER (Dingl. polyt. J., ccix, 7).

STANNIC chloride, as used by the dyers and calico-printers, appears, commercially, in white, crystalline, and more or less solid masses. It is much used in producing scarlet on woollens. It is but seldom pure, containing especially small quantities of iron, and almost always varying quantities of sodium chloride. The iron being positively injurious for scarlets, and not easily removable by the dyers, and the sodium chloride also being objectionable, a simple method is given by which the dyer may prepare his own stannic chloride. Pure stannous chloride is taken, which should not give a blue precipitate with potassium ferricyanide, or white with barium chloride, and this is treated in a porcelain dish with its own weight of pure fuming hydrochloric acid, and then with four times its weight of boiling water. By addition of potassium chlorate in small successive portions to the hot solution, with gentle stirring, the stannous chloride is easily converted into stannic chloride without liberation of chlorine gas. For 1 pound of pure and quite dry stannous chloride, 90 grams of potassium chlorate, at the most, are required. The addition of chlorate is discontinued when the solution, at first clear, turns yellow and begins to liberate chlorine.

W. S.

Finishing Cotton and Linen Goods. (Dingl. polyt. J., ccix, 78.)

INSTEAD of sprinkling with water, it has been recommended to add a hygroscopic salt to the finishing mixture, and calcium chloride is the salt selected as best for the purpose. By hanging the material so prepared for four hours in a cool room, so much moisture is absorbed that it is then ready for calendering. For a mixture of this kind, 100 quarts of the paste and 3 ounces of calcium chloride are recommended.

For the sprinkling process many arrangements have been devised.

By one method the stuff is moistened with water and then placed in a centrifugal machine; by another, steam at a low pressure is caused to impinge against the material, and in condensing, moistens it throughout. The plan most recommended is that in which a rotating brush is used for the sprinkling, the bristles, after passing through a trough of water, having to force themselves past a metal plate, after forcibly passing which, in their rebound to gain their former position, they spirt out the moisture they contain in fine rain.

Finally, a plan has lately been adopted, in which a modification of the well-known "pulverisateur" is used. W. S.

Experiments on the Making of Wine according to Chaptal's Method. By L. MOSCHINI and F. SESTINI (Gazzetta chimica italiana, iii, 195—197).

THE peculiarity of this method is the addition of calcium carbonate to the must after fermentation in the proportion of 0·83 gram to 1 gram of free acid present. The authors, in following it out, found that the free acid of the wine was very nearly neutralized, but that the wine had acquired a disagreeable taste, and became turbid on exposure to the air. Moreover, the proportion of mineral matter was much increased. Further, they find by a series of experiments, that the quantity of calcium carbonate recommended by Chaptal is nearly twice as great as that which is necessary to neutralize the acid, the quantity actually required being only 0·43 gram of pounded Carrara marble for every gram of free acid present. Using this proportion they find that the acidity is corrected, and that the wine thus treated has a very good flavour. H. W.

Meat-flour from Fray-Bentos. By R. POTT (Landw. Versuchs-Stationen, xvi, 193—196).

THIS powdered residue from an extract-of-meat factory is introduced into commerce as a feeding material; its analysis gave the following results:—

Water	10·48
Fat	12·42
Albuminoïds (containing nitrogen 12·01)	72·06
Ash	4·88
	99·84

The total matter soluble in water was 6·18 per cent., which yielded ·64 of ash. The composition of the ash of the meat-flour was as follows:—

K_2O.	Na_2O.	CaO.	MgO.	Fe_2O_3.	P_2O_5.	SO_3.	SiO_2.	Cl.	Sand.	CO_2 and loss.
1·99	1·33	8·79	1·16	5·80	15·33	·82	·66	·31	53·33	7·48

Compared with the ash of fresh beef, this ash appears small in quantity, and very deficient in potash and chlorine, while sand, lime, and iron preponderate. Analysis, in fact, shows that the constituents of the juice of flesh have been removed. R. W.

Parchment Solution. (Dingl. polyt. J., ccvii, 235.)

THIS consists of gutta-percha softened and extended in ether. It furnishes a preservative coating for pictures, cards, &c. Any extraneous matter is easily removed from it by means of a damp cloth. Easily effaceable charcoal and chalk drawings are fixed, if this solution be distributed over their surface in fine spray. The ether evaporates and leaves the gutta-percha, which forms an extremely thin, but protective coating over the design.

W. S.

Sebor's Method of getting Sugar from Molasses (Dingl. polyt. J., ccvii, 410—413).

AN account of some experiments made on a working scale to test the process described in *Dingler's Journal* of 1872, p. 496.

Cleansing of Laboratory Vessels. By J. WALZ (Dingl. polyt. J., ccvii, 427).

VESSELS which have been boiled with oil may be purified by agitation with a dilute solution of potassium permanganate, whereby a film of manganic hydrate is formed, and on washing out with strong hydrochloric acid, chlorine is evolved, which acts decomposingly on organic substances, allowing them to be washed out with water.

W. R.

Cleansing Flasks which have contained Resin Solutions or Essential Oils. (Dingl. polyt. J., ccviii, 79.)

IF the flasks have contained resin solutions, they are to be washed with caustic alkaline leys and finally rinsed with alcohol; if they have contained essential oils, such as oil of turpentine, petroleum, photogene, &c., they are rinsed with one to one and a half ounces of sulphuric acid, and then well washed out in a stream of water.

W. S.

On the so-called Chemical Carbon. By E. KOPP (Dingl. polyt. J., ccvii, 76—77).

THE analysis of a "black," the origin of which is not described; it contained carbon, 80·25 per cent.; elements of water, 15·75 per cent.; ash, 4·0 per cent.

C. H. G.

Use of Size containing Tannic Acid for fixing Aniline Colours (Dingl. polyt. J., ccviii, 397.)

BY the use of tannic acid, mixed with size, the former may be greatly economised, as much less is required to produce a given depth of tint, with size than without it, upon cotton goods.

W. S.

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